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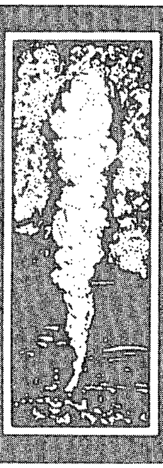

Henry J. Ramey, Jr., Paul Kruger, Frank G. Miller,
Roland N. Horne, William E. Brigham,
and Jon S. Gudmundsson
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GAS CHEMISTRY IN GEOTHERMAL SYSTEMS

Stefán Arnórsson, Science Institute, University of
Iceland, Reykjavík, Iceland
Einar Gunnlaugsson, Reykjavík Municipal District
Heating Service, Reykjavík, Iceland

ABSTRACT

Five new gas geothermometers are introduced. They are useful for predicting subsurface temperatures in water dominated geothermal systems. The geothermometers use data on CO_2, H_2S and H_2 concentrations in fumarole steam as well as CO_2/H_2 and H_2S/H_2 ratios. It is demonstrated that the gas composition of fumarole steam may be used with or without drillhole data to evaluate steam condensation in the upflow zones of geothermal systems. Uncertainty exists, however, in distinguishing between the effects of steam condensation and phase separation at elevated pressures. The gas content in steam from discharging wells and the solute content of the water phase can be used to evaluate which boiling processes lead to "excess steam" in the discharge and at which temperature this "excess steam" is added to the fluid moving through the aquifer and into the well. Examples, using field data, are given to demonstrate all the mentioned applications of geothermal chemistry.

INTRODUCTION

Various aspects of the use of gas chemistry for the exploration for geothermal resources and their development are summarized in this contribution. They are relevant for water dominated reservoirs. The aspects include prediction of subsurface temperatures from the gas content of fumarole steam, estimation of steam condensation in upflow zones and evaluation of boiling mechanisms in aquifers around producing wells. Emphasis is laid on the principles of the different applications but they are elucidated with examples of field data.

THE GAS CONTENT OF WATER IN GEOTHERMAL RESERVOIRS

Geochemical studies during the last few years have demonstrated that gas concentrations and gas ratios in drillhole discharges correlate with the undisturbed temperature of the producing aquifers (Giggenbach, 1980; D'Amore and Panichi, 1980; Nehring and D'Amore, 1981; Arnórsson et al., 1983). It has further been demonstrated that the fugacities of CO_2, H_2S and H_2 are buffered by hydrothermal mineral assemblages (Arnórsson and Gunnlaugsson, 1983). Arnórsson et al. (1983) proposed temperature functions for CO_2 and H_2S which are valid up to 250°C. Giggenbach (1980) and Arnórsson (1983) have expressed temperature functions in terms of gas pressures for CO_2 and CO_2, H_2S and H_2 respectively in geothermal waters. Table 1 gives temperature functions for CO_2, H_2S and H_2 concentrations in geothermal waters which are valid up to 350°C as indicated.

Alteration processes in geothermal systems involve dissolution of the primary rock constituents and precipitation of new ones via transfer of matter through the aqueous phase. Which new minerals are precipitated depends on the temperature of the water, kinetic factors and the composition of the rock, or better the composition of the geothermal system. It is a well known problem in metamorphic geology that different minerals or mineral assemblages have similar solubilities. This implies that different minerals will often produce similar aqueous solute concentrations for compatible components at equilibrium. Compatible components are those incorporated in mineral phases. This is well demonstrated by the results of Bird and Norton (1981) on the Salton Sea geothermal system. A mineral zonation is observed with depth in that system and each zone is characterised by a particular mineral assemblage. Chemical thermodynamic calculations show that any of these assemblages give about the same fluid composition (the observed composition) at equilibrium for the compatible components. Yet, in strict terms, it is very important to realise that the temperature functions given in Table 1 are valid only for certain mineral assemblages, assemblages which form when volcanic rocks of basic to acidic composition are altered because they have been derived from data from geothermal systems located in such rocks. These temperature functions may not be valid for geothermal systems located in other rock types, particularly if their composition differs much from the mentioned rock types. Alteration may lead to the formation of different mineral assemblages that would buffer gas fugacities at a significantly different level at any temperature.

For H_2S and H_2 two functions are presented in Table 1, each valid over a fixed range of water

Table 1. Temperature functions for gas concentrations (as log moles) in geothermal reservoir waters.

Gas		Temperature function (^{o}K)	Remarks
CO_2	-1.09	$-3894.55/T + 2.532 \cdot \log T$	All waters
H_2S	-11.80	$-0.06035 \cdot T - 17691.09/T + 27.163 \cdot \log T$	All waters above 300°C and waters in the range 200-300°C if Cl>500ppm
H_2	-3.04	$-10763.54/T + 7.003 \cdot \log T$	
H_2S	-1.24	$-4691.84/T + 2.830 \cdot \log T$	All waters below 200°C and waters in the range 200-300°C if Cl<500ppm
H_2	+11.96	$+0.08489 \cdot T + 8254.09/T - 27.587 \cdot \log T$	

salinity and temperature. Water salinity may to some extent reflect rock type. Different rock types have different concentrations of the incompatible component chloride and it is the availability of this component which governs water salinity.

It has not been established which minerals control CO_2, H_2S and H_2 fugacities as described by the functions in Table 1 below some 200-250°C. At higher temperatures the assemblage epidote-prehnite-calcite-quartz seems to control CO_2 levels. For water containing less than 500 ppm chloride and below 300°C pyrite, pyrrhotite, epidote and prehnite appear to buffer H_2S and H_2 fugacities but pyrite, epidote, prehnite and magnetite or chlorite seem to be involved in the case of waters containing over 500 ppm chloride.

GEOTHERMOMETRY

The drillhole data on which the functions in Table 1 are based have been used to calibrate several gas geothermometers. The application of these gas geothermometers involves the sampling and analysis of fumarole steam and derivation of subsurface temperatures with the aid of the functions in Table 2. These functions refer to gas concentrations in steam at atmospheric pressure and assume adiabatic boiling of the parent water and equilibrium degassing (Arnórsson and Gunnlaugsson, 1983). Condensation of steam in the upflow and phase separation at pressures above atmospheric cause high temperature estimates for the CO_2, H_2S and H_2 geothermometers as they are based on concentration in steam. On the other hand the geothermometers which use gas ratios (CO_2/H_2 and H_2S/H_2) are not significantly affected by these processes as the dissolved gases are practically quantitatively transferred to the steam phase already at the early stages of boiling. The geothermometers which use gas concentrations are advantageous over the gas ratio geothermometers when steam condensation or phase separation produces less deviation from the adiabatic boiling model adopted than gas reactions in the upflow. Arnórsson and Gunnlaugsson (1983) have demonstrated, by comparing measured temperatures in wells and data from fumaroles, that the predicted geothermometry temperatures compare generally well with the temperatures actually encountered in drillholes at depths as great as 1000 m or more. Their work shows that H_2S and to a lesser extent H_2 tend to be removed from the steam in the upflow presumably as a result of reactions with alteration minerals in the wall rock or oxidation. Therefore CO_2/H_2 ratios may be regarded to yield conservative estimates of subsurface temperatures as this ratio increases with decreasing temperatures as may be seen the respective temperature functions in Table 2. CO_2 temperatures can be expected to be on the high side as this gas does not seem to be lost from the steam in the upflow. H_2S and H_2 temperatures are often intermediate between the CO_2/H_2 and the CO_2 temperatures as the effect of condensation is counterbalanced to a greater or lesser extent by the removal of these gases from the steam in the upflow. H_2S/H_2 temperatures yield high values when H_2S has been removed preferrentially to H_2 in the upflow.

Data from fumaroles in Hveragerdi are used here as an example to illustrate gas geothermometry results (Fig.1). Many wells have been sunk in this area which forms the southernmost part of the Hengill geothermal field in southwest Iceland. Xi-Xiang (1980) has recently summarized the temperature distribution in the Hveragerdi reservoir from measurements in wells. In general temperature increases northwards from about 150°C in the village of Hveragerdi to 230°C in the far north in well 1 (Fig. 1). A temperature maximum is observed in most wells which has been interpreted by lateral flow from the central part of the Hengill geothermal field (Árnason et al., 1968).

For convenience for discussing and comparing measured temperatures in wells and gas geothermometry temperatures the Hveragerdi field is divided into two areas, one around wells 2, 4 and 5 and the other at the head of the valley running north from Hveragerdi where wells, 1, 3, 6, 7 and 8 are located. Here fumaroles are concentrated on high ground on the northern valley slopes, and in smaller V-valleys dissecting these slopes.

Table 2. Temperature functions for gas geothermometers. Gas concentrations are in mmoles per kg og steam.

Geothermometer	Temperature function	Mean dev. °C	Standard dev. °C	Remarks
CO_2	$-44.1 +269.25Q -76.88Q^2 +9.52Q^3$	20[a]	21[a]	All waters
H_2S	$+246.7 +44.81Q$	14	9	All waters above 300°C and waters in the range 200-300°C if chloride >500 ppm.
H_2	$+277.2 +20.99Q$	5	6	
CO_2/H_2	$+341.7 -28.57Q$	14	8	
H_2S/H_2	$+304.1 -39.48Q$	11	5	
H_2S	$+173.2 +65.04Q$	15	13	All waters below 200°C and waters in the range 200-300°C if chloride <500 ppm.
H_2	$+212.2 +38.59Q$	19	14	
CO_2/H_2	$+311.7 -66.72Q$	28	23	

Q designates the logarithim of the respective gas concentration or the gas ratio.
[a] Data points with aquifer temperatures below 150°C were omitted.

CO_2/H_2 temperatures for fumaroles around wells 2, 4 and 5 are in the range 117-172°C but CO_2 temperatures range from 237° to 255°C. These temperatures are to be compared with the range 161-198°C measured in the nearby wells. According to earlier statement the highest CO_2/H_2 temperatures should be regarded as a conservative value for subsurface temperatures and CO_2 temperatures are possibly too high. For the upper area maximum CO_2/H_2 temperature is 233°C but the highest recorded downhole temperature is 230°C in well 1. CO_2 temperatures range from 257° to 278°C.

Inspection of Fig. 1 reveals that H_2 temperatures tend to lie inbetween the CO_2 and CO_2/H_2 temperatures. CO_2 concentrations do not change as rapidly with temperature as do H_2 concentrations according to the gas geothermometry functions. Therefore the discrepancy between the CO_2, H_2 and CO_2/H_2 geothermometry results can be explained by steam condensation/phase separation et elevated pressure or removal of H_2 from the steam in the upflow or a combination of these processes.

H_2S temperatures compare well with H_2 temperatures in the lower area. However, in the upper area they tend to be lower and also lower than the CO_2/H_2 temperatures. In the upper area the fumaroles are mostly located on high ground and well above the water table. According to Arnórsson and Gunnlaugsson (1983) H_2S is particularly prone to be removed from the steam under conditions of low water table.

EVALUATION OF CONDENSATION

The discrepancy between the CO_2/H_2 geothermometry results on one hand and the CO_2 or H_2 results on the other hand may be used to evaluate steam condensation in upflow zones of geothermal systems. The evaluation involves calculation of CO_2 or H_2 concentrations from the CO_2/H_2 temperature and the respective functions in Table 2. The ratio of the calculated CO_2 (or H_2) concentration divided by the analysed concentration equals the fraction of steam, Y, which has not condensed and (1-Y), is therefore the condensed fraction. Since H_2 tends to be removed in the upflow, CO_2/H_2 temperatures tend to be low giving high values for (1-Y). For the Hveragerdi fumaroles (Fig. 1) this method indicates that 59-95% of the steam has condensed in the upflow and 77% on average.

Another method to estimate condensation involves comparison between the gas content in fumaroles and in steam discharged from wells at atmospheric pressure. Using CO_2 data from wells 2 and 4 (aquifer temperatures 182° and 181°C) condensation is indicated which amounts on average to 73% in the lower area, the range being 65-79%. The same approach for the upper area using well 7, with aquifer temperature of 225°C, give a range of 68-84%, the average being 77%.

Although numerous boiling hot springs occur in the Hveragerdi area, it may be that the discrepancy between the gas concentrations in fumarole steam and in steam from wells after the discharge has flashed to atmospheric pressure is not due to condensation but to separation of the steam from the water in the upflow at pressures above atmospheric. Study of fumarole chemistry in several geothermal fields in Iceland by Arnórsson and Gunnlaugsson (1983) shows that there is some relation between the discrepancy between CO_2 (and H_2) temperatures on one hand and CO_2/H_2 temperatures on the other and the age of the rocks. The difference tends to be largest in the oldest rocks. It is generally accepted that the permeability of the volcanic rocks in Iceland decreases with time due to compaction and hydrothermal alteration. It is to be

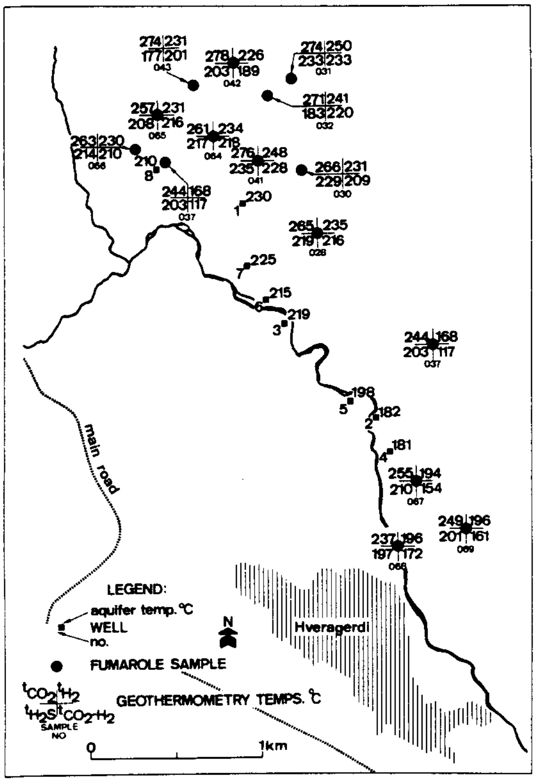

Fig. 1. Gas geothermometry results for the Hveragerdi area, southwest Iceland.

expected that low permeability in upflow zones where boiling occurs will favour phase separation. It is concluded that fumarole chemistry can be affected by both steam condensation and phase separation but further study is required to evaluate the relative magnitude of these processes in different fields. The results may contribute to early evaluation of permeability in geothermal systems but also to estimation of natural heat loss.

EVALUATION OF BOILING PROCESSES

It is often observed that the enthalpy of wet-steam well discharges varies with wellhead pressure but also with time, generally towards increasing steam to water ratios. As far as the present authors know discharge enthalpy changes are confined to wells fed by a two phase mixture of water and steam. Changes in the fluid chemistry (or lack of changes) which accompany discharge enthalpy changes can be useful in evaluating the processes which are involved. Results pertinent to this aspect of applied geochemistry have been described by Arnórsson (1981), Glover et al. (1981) and Grant and Glover (1983).

Steam is excess of that formed by adiabatic boiling of water of a particular aquifer temperature is here termed "excess steam".

It is visualized that "excess steam" in wet-steam well discharges may be the outcome of either of two processes, or a combination of them. One of these processes involves phase separation in the aquifer and preferrential movement of the steam into the well. The other process involves evaporation of pore water as a result of heat transfer from the rock to the fluid. Pressure drop caused in the aquifer around a producing well will cool the fluid by boiling and initiate heat transfer from the rock.

In the present contribution it is demonstrated how fluid chemistry may be used to evaluate the relative magnitude of these two processes for individual wells. The evaluation makes use of both gas composition and solutes in the aqueous phase. Data from Nesjavellir, Iceland and Olkaria, Kenya, are used to elucidate this application of chemistry.

If relative permeability is the cause of high discharge enthalpy, i.e. "excess steam", it is to be expected that the concentrations of gases in the steam phase at a particular pressure remain constant despite changes in the discharge enthalpy. If, on the other hand, evaporation of pore water was responsible, it is to be expected that gas concentrations in the total discharge would remain constant and the gas content of the steam phase would thus decrease in proportion to the amount added of pore water derived steam. It is logical to assume that the pore water would become degassed during the early stages of boiling and further evaporation would yield practically gas free steam.

The data on CO_2 from well 6 at Nesjavellir, Iceland (Fig. 2) indicates that the relative permeability effect is for all practical purposes the sole cause of the increased discharge enthalpy from 1290 to 2140 J/g that occurred during one week after the well was discharged for the first time (see Stefánsson et al., 1983).

The temperature, or more accurately the enthalpy, of the "excess steam" added may affect evaporation of the water fraction in well discharges. If the steam is added at a pressure close to the sampling pressure, i.e. close to the well, the addition will not affect the aqueous solute concentrations. If, on the other hand, the steam is added at a significantly different pressure so that its enthalpy differs markedly from that of steam at the sampling pressure, its presence and relative amount will affect the evaporation of the discharged water.

Fig. 3 shows variation in silica and sodium concentrations in the water discharged from well 6 at Nesjavellir with discharge enthalpy during the first week of flow. The horizontal lines represents expected relative concentrations if the "excess steam" was added at a pressure equal to the sampling pressure but the curves represent calculated relative solute concentration variations if the steam was added

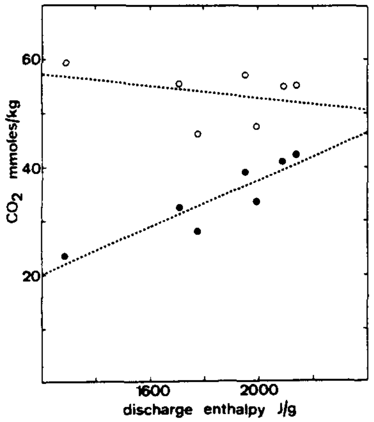

Fig. 2. CO_2 concentrations in well 6 at Nesjavellir during the first week of discharge in December, 1982. Filled symbols designate concentrations in the total discharge and open symbols concentrations in the steam at atmospheric pressure.

at 290°C, i.e. the undisturbed temperature of the dominant feeder. The results for sodium favour that the "excess steam" was added at 290°C but silica concentrations do not. It is possible that the silica concentrations do not give a reliable picture of the situation. They are sensitive to temperature variations in the formation. Initial silica concentrations are low but later they correspond well with the aquifer temperature of 290°C assuming equilibrium with quartz.

Data on the composition of water and steam from wet-steam wells may not be sufficiently complete to permit correlation of possible chemical changes with changes in discharge enthalpy. A single analysis of the steam fraction and measurement of the discharge enthalpy may be tentatively used to evaluate the relative magnitude of the two boiling processes in the aquifer with the aid of the equations in Table 1. If evaporation of pore water only was responsible for the "excess steam" in a well discharge, the gas content of the total discharge should be equal to that described by the respective functions in Table 1 at a specified aquifer temperature. If the relative permeability effect was the cause of "excess steam", the gas content in the steam phase of the discharge multiplied by calculated steam fraction equal to that obtained by adiabatic boiling should conform with the functions in Table 1.

Fig. 4 shows data on the gas content in steam from selected wells at Olkaria in Kenya. The spread of data points indicates that wells with the lowest Na-K geothermometry temperatures owe their "excess steam" dominantly to phase separation but for wells with Na-K temperatures significantly over 240°C pore water evaporation appears to dominate. A steam zone of 240°C caps a boiling water reservoir at Olkaria (Svanbjörnsson et al., 1983). The wells which have Na-K temperatures significantly higher than 240°C are dominated by feeders in the boiling water reservoir but wells with Na-K temperatures of 240°C of somewhat less appear to be dominantly fed from the steam zone. It can be noted from Fig. 4 that the gas content of all the wells are very similar and correspond rather closely with gas geothermometry temperatures of 240°C. It is a plausible explanation, although considered unlikely in view of flow characteristics of wells (see Svanbjörnsson et al., 1983), that the steam in the well discharges is dominantly derived from the steam zone and Na-K temperatures reflect some water inflow from variable depths within the boiling water reservoir.

QUALITY OF STEAM

The gas content of steam at a particular separation pressure may be predicted in the case of CO_2, H_2S and H_2 with the use of the equations in Table 1. Usually these gases constitute far the larger part of the total gas in geothermal fluids although CH_4 and N_2 may

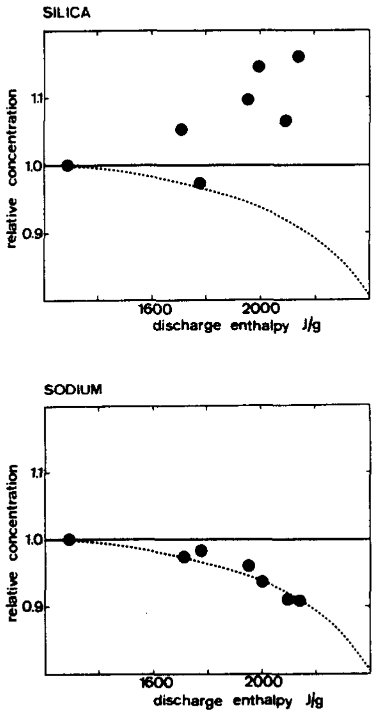

Fig. 3. Relative changes with discharge enthalpy in the silica and sodium concentrations in water (at atmospheric pressure) from well 6 at Nesjavellir. Straight lines correspond with concentrations, if the "excess steam" was added at a pressure equal to the sampling pressure but curves if steam at 290°C (the aquifer temperature for the well) was added.

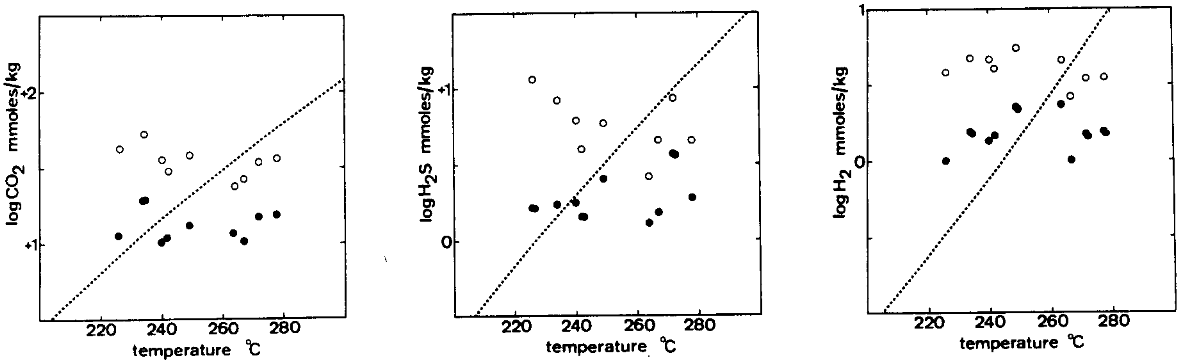

Fig. 4. CO_2, H_2S and H_2 concentrations in fluid discharged from wells at Olkaria. Open symbols represent actual concentrations in the total discharge and correspond therefore with the "excess steam" being derived from evaporation of degassed pore water. Filled symbols show calculated concentrations in the reservoir water on the assumption that the "excess steam" in the discharges was caused by phase separation in the aquifer and preferrential movement of the steam into the wells. The curves designate gas concentrations in equilibrated geothermal reservoir waters according to Table 1. The data are from Muna (1982).

sometimes contribute significantly. The steam fraction, X, formed by adiabatic boiling of water equals $(h-h_p)/L_p$ where h and h_p represent the enthalpies of steam saturated water at a specified aquifer temperature and the enthalpy of water at steam pressure respectively. L_p is the latent heat of vaporization at that pressure. By dividing X into a calculated gas concentration derived from the equations in Table 1 the gas concentrations in the steam are obtained. This is the maximum anticipated concentration in the steam phase. If increased well discharge enthalpy was caused by phase separation in the aquifer, the gas content in the steam would not change and therefore stay at the theoretical maximum level. Pore water evaporation, as a cause of increased discharge enthalpy, would on the other hand lower gas concentrations from this maximum. As an example it can be mentioned that gas $(CO_2+H_2S+H_2)$ in steam at 6 bars abs. calculates to be 0.35 and 1.1% by volume at maximum for aquifer temperatures of 250°C and 300°C respectively. For a discharge enthalpy of 2200 J/g and pore water evaporation the corresponding figures are 0.10% and 0.48% respectively. It is considered to be useful to predict the quality of geothermal steam with respect to gas content already at the geochemical survey phase in geothermal exploration. This can be done by making use of estimated subsurface temperatures using geothermometry.

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