



## **GAS GEOCHEMISTRY OF THE MIRAVALLS, PAILAS AND BORINQUEN GEOTHERMAL AREAS OF COSTA RICA, AND A COMPARISON WITH REYKJANES AND THEISTAREYKIR GEOTHERMAL FIELDS, ICELAND**

**Bi Yun Zhen-Wu**

Instituto Costarricense de Electricidad - ICE  
Centro de Servicio Recursos Geotérmicos  
Apartado 10032-1000, San José  
COSTA RICA, C.A.  
*biyzen@ice.go.cr*

### **ABSTRACT**

The application of gas geochemistry is an integral tool in geothermal development, providing information that is not obtainable by geological or geophysical surveys. The objectives of this study were to interpret deep fluid gas composition with the purpose of understanding gas behaviour in a geothermal system, and to evaluate the applicability of gas geothermometers for geochemical exploration and exploitation. Both well and fumarole gas samples from three Costa Rican geothermal areas (Miravalles, Pailas and Borinquen) and two Icelandic high-temperature (between 230 and 310°C) geothermal fields (Reykjanes, SW-Iceland, and Theistareykir, NE-Iceland) were considered. About 21 single gas and gas ratio geothermometers were applied. Equilibria of mineral assemblage buffers that could potentially control aquifer partial pressure of hydrogen sulphide (H<sub>2</sub>S), hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) were modelled. The origin of gases was identified with a ternary N<sub>2</sub>-CO<sub>2</sub>-Ar diagram. Validation of geothermometers was carried out by comparing the salinity and redox state of the geothermal systems with those conditions in which the gas geothermometers were calibrated. Three mineral assemblage buffers could control the aquifer H<sub>2</sub>S and H<sub>2</sub> partial pressures in Miravalles neutral and Reykjanes geothermal systems. These assemblages are: anhydrite-clinozoisite-magnetite-prehnite-pyrite-quartz, anhydrite-magnetite-pyrite-quartz-wollastonite and hematite-magnetite-pyrite. Aquifer H<sub>2</sub>S and H<sub>2</sub> partial pressures in Theistareykir system could be controlled by two mineral buffers: epidote-pyrrhotite-pyrite-prehnite and magnetite-pyrrhotite-pyrite. Single H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> geothermometers calibrated for saline fluids (>500 ppm chloride) are appropriate for Miravalles neutral and Reykjanes systems, whereas those calibrated for dilute fluids (<500 ppm chloride) are suitable for the Theistareykir system. Gas ratio geothermometers are more appropriate for application in fumaroles than single gas thermometers due to steam condensation. Both single gas and ratio geothermometers should be used as complementary tools in a geochemical assessment during geothermal exploration and reservoir management.

## 1. INTRODUCTION

Pioneers, such as A.J. Ellis, W.A.J. Mahon, Don White, Robert Fournier, Harold Helgeson, Alfred Truesdell, Stefán Arnórsson, Franco D'Amore and Werner Giggenbach laid the foundation for modern geothermal geochemistry more than 30 years ago (Klein, 2007). Since that time most geothermometers based on non-condensable gases have been developed. However, due to the complexity and diversity of the techniques developed by these contributors, the application of gas geochemistry to the geothermal development is still viewed with reserve (Powell, 2000).

Geothermal gases carry an imprint of deep conditions since they escape from the original source to the surface (Giggenbach, 1991). Gas concentrations and gas ratios have been used as geothermometers using both well and fumarole data (Giggenbach, 1981). Therefore, applications of gas geochemistry are valuable and essential geochemical tools and should play a key role during geothermal exploration, resource evaluation, and not least for reservoir management (White, 1970).

The 1970s oil and energy crisis promoted the development of geothermal resources for commercial electricity exploitation in Costa Rica (Fallas and Rodríguez, 2010). Investigations to assess the geothermal potential of the Guanacaste Province were started in 1975 by the Instituto Costarricense de Electricidad (ICE), a public entity that deals with the national production and distribution of electricity. Four years later, the Miravalles area was the first to be explored in the country (Mainieri et al., 1985). Electricity generation from geothermal energy began in this field in 1994, when the first 55 MWe unit was commissioned. The total installed capacity of this field is now 165.5 MWe, which is equivalent to 8% of the total electrical capacity of Costa Rica. Energy production at Miravalles amounts to about 13% of the total energy produced by the country's electrical system (Mainieri, 2010).

Northwest of the Guanacaste volcanic range, specifically at the Rincón de la Vieja volcanic complex, two important zones, Pailas and Borinquen, were identified by prospective studies. At Pailas geothermal field, the initial 41 MWe binary plant is under construction, and the Borinquen geothermal area is under exploration. The information obtained from drilling an exploratory well confirmed the presence of an important thermal anomaly associated with the magma chamber of the aforementioned volcano (Mainieri, 2010).

Costa Rica's goal is to become carbon-neutral by 2021. About 25% of the country is comprised of environmentally protected areas. Most of the potential geothermal resources of the country are located within the protected areas (Fox, 2010). The environmentally friendly development of these geothermal areas requires more precise exploration methods. Thus, the application of geochemical techniques, basic inexpensive sampling and analysis, is an integral part of any geothermal prospecting and management of a field, providing information that is not obtainable by geological or geophysical surveys (Giggenbach, 1991; D'Amore, 1991).

The present study's objectives are to interpret deep fluid gas composition with the purpose of understanding the gas behaviour in a geothermal system, and to evaluate the applicability of gas geothermometers as tools for geochemical exploration and exploitation. Costa Rican geothermal areas (Miravalles, Pailas and Borinquen) and Icelandic high-temperature geothermal fields (Reykjanes, SW-Iceland, and Theistareykir, NE-Iceland) were compared.

## 2. GEOTHERMAL AREAS OF COSTA RICA

Costa Rica is located in the southern part of Central America, in the zone of interaction between the Cocos and Caribbean plates that has generated an internal magmatic arc, in which the Guanacaste volcanic cordillera comprises the northwest segment (Vega et al., 2005; Figure 1). The magmatic arc

of the Guanacaste volcanic cordillera is constituted by Tertiary and Quaternary volcanic rocks. The Tertiary rocks form an andesitic volcanic plateau with abundant pyroclastites and ignimbrites alternating with detrital sediments. The Quaternary rocks are mainly lavas related to the strato-volcanoes: Orosí, Rincón de la Vieja, Miravalles and Tenorio volcanoes (Mora, 1989). On the Pacific side, there are four promising thermal fields: Borinquen, Hornillas, Pailas and San Jorge-Santa María, which are aligned in a NW-SE direction, parallel to the axis of the Rincón de la Vieja volcano (Molina, 2000).

So far, only Miravalles geothermal field is being commercially exploited; Pailas geothermal field is in development, and Borinquen geothermal area is in the exploration stage.

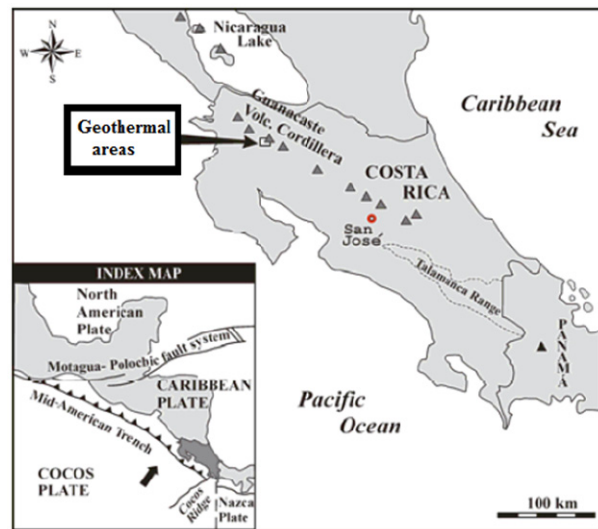


FIGURE 1: Location of Costa Rica, Central America (Modified from Vega et al., 2005)

## 2.1 Miravalles, Pailas and Borinquen geothermal areas

The Miravalles geothermal system is a high-temperature (230-240°C) liquid-dominated reservoir (Gherardi et al., 2002). It is located inside a caldera about 15 km in diameter known as Guayabo Caldera, whose formation was related to successive explosions with deposition of pyroclastic flows originated from a shallow magma chamber of less than five kilometres (Chiesa et al., 1992). The geothermal reservoir is located below about 700 m depth with temperatures decreasing to the south and west (Vallejos, 1996). About 53 deep wells have been drilled, 33 production wells, and 14 gravity injection wells for residual waters in two different areas: the primary area is located to the south, and a secondary one is west of the production area (Mainieri, 2010).

The Pailas geothermal field is located southwest of the Rincón de la Vieja volcano. This field is situated inside the Guachipelín caldera structure, which is inside an older and bigger caldera structure known as Cañas Dulces Caldera. It seems that its heat source reservoir is associated with the Rincón de la Vieja volcano (Chavarría et al., 2010). So far, five vertical and three directional wells have been drilled in this field; drilling will continue through 2011.

The Borinquen geothermal area is located west of the Rincón de la Vieja volcano. Prospective studies were carried out in the area 30 years ago by ICE. Twenty exploratory wells and two deep wells were drilled in the area, and confirmed the existence of a high-temperature geothermal reservoir. The studies suggested that the heat source is located to the northeast, towards the aforementioned volcano (Mora et al., 2006).

### 2.1.1 Lithostratigraphy

Miravalles and Rincón de la Vieja are andesitic volcanoes, with mostly basalt and andesitic lava flows (Chiesa et al., 1994). The rock sequence within and around the Guayabo caldera, site of the Miravalles geothermal field, includes a series of stratigraphic units related to processes that occurred before, during and after the formation of the caldera. These units include pyroclastic materials, lavas, debris, avalanches and lacustrine deposits. The stratigraphic units are known as: deep lava unit, ignimbrite unit, lava-tuff unit, Río Liberia formation, volcano sedimentary unit, dome-flow unit, Cabro Muco andesitic unit, post Cabro Muco unit, fluvio-lacustrine unit, and recent deposits unit. The Cabro Muco andesitic unit includes mainly andesites and basaltic-andesites, as well as sporadic lithic

tuff levels; this unit has been reported in a majority of the wells with thicknesses between 50 and 1000 m (Vega et al., 2005).

Pyroclastic flows are the predominant rock type in the Pailas area (Molina, 2000). The drilled sequences vary from andesitic-basalt to rhyolitic composition and are associated with pyroclastic and effusive activity from ancient volcanic edifices (Chavarría et al., 2010). The lithostratigraphic column includes six separate volcano-stratigraphic units which are correlated to regional formations dating from Miocene to Holocene: Aguacate group, Bagaces group, Liberia formation, domes unit, Pital formation, and recent products unit. Of these formations, the only unit not represented in an area outcrop is the Aguacate group. From deep well data, the geothermal reservoir seems to be restricted to the basal section of the Bagaces group and the Aguacate group (Chavarría et al., 2006).

Bonrinquen area is constituted mainly by explosive low permeability volcanic rocks. In general, these rocks presented an altered vitreous matrix. From the most ancient to the most recent, the stratigraphic sequence is composed of four groups: Bagaces group, Liberia group, Pital formation and Rincón de la Vieja volcano unit. The sequence may indicate an increase in lava northeast of the Borinquen area, possibly related to the activity of an ancient volcano (Mora et al., 2006).

### 2.1.2 Alteration mineralogy

The primary mineralogy of Miravalles consists of intermediate composition plagioclase, pyroxene (augite and hypersthene), magnetite and accessory quartz and apatite. The hydrothermal mineralogy shows a progressive change, indicative of increasing temperature with an increase in depth (Rochelle et al., 1989). This field is composed of a high-enthalpy reservoir that is divided into three hydrothermal alteration zones (Figure 2) based on the dominant clay mineral species: the smectite, transition and illite zones. The smectite zone (<165°C) corresponds to the most superficial part of the field (upper level of the cap rock) and is characterised by the presence of clays from the smectite group along with iron oxide/hydroxides and the appearance of subordinate pyrite, calcite, chlorite, zeolites, and some forms of silica. The transition zone is defined by the appearance of mixed-layer clays, illite/smectite. The illite zone is associated particularly with reservoir levels with temperatures of at least 220°C and is characterised by the presence of illite, higher percentages of epidote and well-crystallized chlorite minerals (Vega et al., 2005). On the other hand, Chavarría (2003) has suggested that anhydrite and calcite are present in both neutral and acid wells at Miravalles. He also concluded that acid fluids are not in equilibrium with the alteration mineralogy, probably due to the short time of residence.

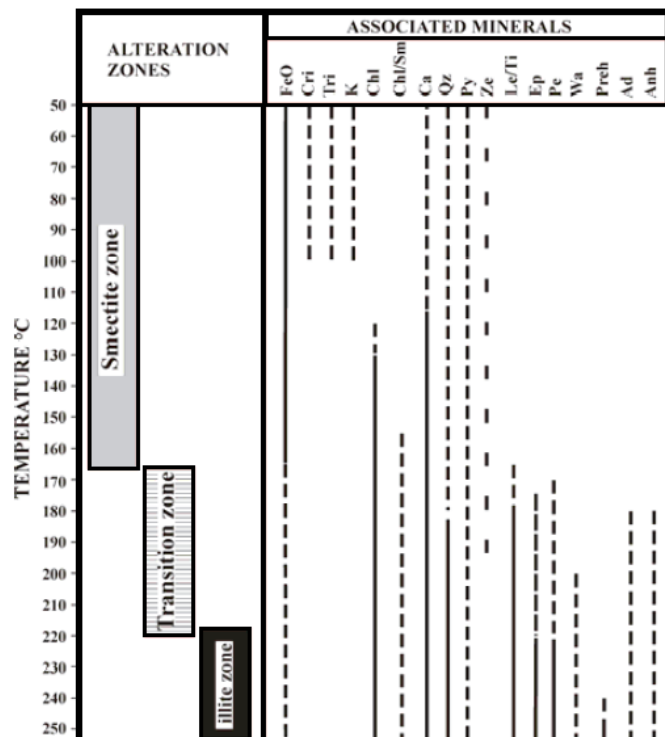


FIGURE 2: Clay alteration zones and associated mineralogy of the Miravalles geothermal field. FeO: iron oxides/hydroxides; Cri: cristobalite; Tri: tridominte; K: kaolinite; Chl: chlorite; Chl/Sm: Mixed-layer clays - Chlorite, Smectite; Ca: calcite; Qz: quartz; Py: pyrite; Ze: zeolite; Le/Ti: leucoxene/titanite; Ep: epidote; Pe: peninne; Wa: wairakite; Preh: prehnite; Ad: adularia; Anh: anhydrite (modified from Vega et al., 2005)

The rocks in the Pailas area are altered, mainly to clays (smectite and kaolinite), and in some places sulphur deposits and iron oxides occur. The kaolinite is a product of hydrothermal alteration (Molina, 2000). The Pailas secondary mineralogy is composed of clays (smectite and illite), quartz, calcite, chlorite, sericite, leucoxene, epidote, zeolite and wairakite. Two alteration zones were identified in the Pailas and Borinquen fields: a low-temperature zone and a high-temperature zone (Chavarría et al., 2006; Mora et al., 2006)

### 2.1.3 Fluid chemistry

At Miravalles there are four different geothermal aquifers: a shallow steam-dominated aquifer located in the northeast part of the field (Vallejos, 1996), and: a) a neutral sodium-chloride aquifer (Na-Cl), located in the northern and central sectors of the field; b) a neutral sodium-chloride-bicarbonate aquifer (Na-Cl-HCO<sub>3</sub>), located in the southeast sector of the field; and c) an acid sodium-chloride-sulphate aquifer (Na-Cl-SO<sub>4</sub>), located in the northeast sector of the field (Sánchez, et al., 2005; González et al., 2006). The bulk of the production is from the neutral NaCl aquifer. The non-condensable gas content at Miravalles ranges from 0.4 to 1.2 % w/w. Since its exploitation, these gases have been increasing rapidly in the northern part of the production zone, mainly due to pressure decline of the reservoir. Some strategies have been applied: an increase of injected fluid volume in the western sector, and a change in the production rate of the northern wells at a minimum flow (Moya and Sánchez, 2005).

In the Pailas geothermal field, no chloride springs associated with fluid discharge from the reservoir were found. Sulphate hot springs were found in a NW-SE direction along the volcanic range, whereas bicarbonate springs were found in a NE-SW direction. The fluid of the wells is characterised as sodium-chloride type, pH neutral, with high salinity (from 12,000 to 13,000 ppm of TDS), and a low content of gases as well as non-condensable gases (<0.1 %w/w) (Chavarría et al., 2006).

At Borinquen area, superficial hydrothermal manifestations at the intersection of different structures may indicate that E-W and NE-SW regional systems dominate deep circulation of fluids. Geothermal fluid distribution is controlled by secondary permeability, where tectonic structures are important. Sulphate (from 48 to 422 ppm), bicarbonate (from 73 to 300 ppm) and chloride (from 2,960 to 3,035 ppm) waters have been found in the studied area. Chloride type springs were the manifestations located at Salitral Norte. Solute geothermometers indicated reservoir temperatures between 216 and 230°C (Mora et al., 2006).

## 3. GEOTHERMAL FIELDS IN ICELAND

Iceland is located on the Mid-Atlantic Ridge, which is the boundary between the North-American and Eurasian tectonic plates. As a result of its location, Iceland is one of the most tectonically active places on Earth and, therefore, has a huge geothermal potential. In the high-temperature (>200°C) fields, geothermal steam is utilised for electricity generation and in some cases for co-generation plants. The low-temperature (<150°C) fields are used mainly to supply hot water for district heating (Ragnarsson, 2010).

### 3.1 Reykjanes and Theistareykir geothermal fields

Reykjanes high-temperature geothermal field (Figure 3) is located at the southwest tip of the Reykjanes Peninsula, SW-Iceland, about 50 km southwest of Reykjavík. A geothermal power plant of 100 MWe started operation in 2006, and an expansion of the plant by 80 MWe is under preparation (Ragnarsson, 2010). On the other hand, Theistareykir is a high-temperature geothermal field located in northeast Iceland, about 25 km northwest of Krafla geothermal field. This field has not yet been

utilised. A consortium of Icelandic energy companies has already drilled six exploratory wells in the area. It is estimated that they could be used for the production of about 45 MWe (Ragnarsson, 2010).

### 3.2 Lithostratigraphy

Rocks of both Reykjanes and Theistareykir geothermal areas are predominantly basaltic. At Reykjanes area, the stratigraphy can be divided into four main units. The strata range from probable pillow basalt formations at the deepest level to shallower tuffaceous volcanic successions intercalated with shallow marine fossil-rich sediments, and lastly pillow basalt and subaerial lavas (Franzson et al., 2002). Reservoir rocks of Theistareykir area are mainly tholeiitic basalt lavas and hyaloclastites, with the occasional occurrence of acidic volcanic rocks that are moderately to highly altered (Marosvölgyi et al., 2010).



FIGURE 3: Location of Reykjanes and Theistareykir high-temperature geothermal fields in Iceland (modified from Freedman et al., 2009)

### 3.3 Alteration mineralogy

In high-temperature geothermal areas ( $>200^{\circ}\text{C}$ ) in Iceland, the alteration minerals formed show regular zoning with increasing temperature: smectite, chlorite, epidote and actinolite (Sveinbjörnsdóttir, 1992). Alteration minerals of well RN-10 in Reykjanes geothermal field include calcite, quartz, epidote, wollastonite, garnet, anhydrite, pyrite, chlorite and albite (Franzson et al., 2002). These same minerals were found in well RN-17, in addition to titanite and actinolite (Marks et al., 2010).

The alteration pattern at Theistareykir suggests a steadily increasing temperature with depth as well as volume of intrusions (Ármansson, 2008). Several alteration minerals have been identified at Theistareykir, including smectite, chlorite, mixed layer chlorite/smectite, laumontite, mordenite, wairakite, pyrite, pyrrhotite, and quartz (Marosvölgyi et al., 2010; Gudmundsson and Arnórsson, 2004).

### 3.4 Fluid chemistry

Although both Reykjanes and Theistareykir systems have the same sequence of alteration minerals, the actual composition of the minerals differs between the systems, reflecting the different chemical composition of the circulating waters (Sveinbjörnsdóttir, 1992). The Reykjanes system is fed with sea water (19,000 ppm Cl) while the Theistareykir system is fed by meteoric water and has low salinity ( $<500$  ppm Cl) (Stefánsson and Arnórsson, 2002; Ármansson, 2008). The most important deviations from sea water chemistry are magnesium and sulphate depletion and an increase of silica, potassium and calcium concentrations, all to be expected at high temperatures (Fridleifsson et al., 2003).

## 4. GAS GEOCHEMISTRY

Geothermal water and steam discharged at the surface, such through fumaroles, hot springs or well discharges, provide information about reservoir conditions and processes, due to the fact that they “have been there” and generally carry imprints of their deeper histories with them (Giggenbach, 1991). With a geochemical model, it is possible to use the gas composition of the fluid collected at surface to calculate reasonable values of some reservoir parameters, such as temperature, steam fraction, partial pressure of gases and its redox conditions, in a wide variety of geothermal fields (D’Amore, 1991).

### 4.1 Origin of geothermal gases

Geothermal gases are derived from high-temperature reactions within a reservoir or are introduced with recharge water (Nehring and D’Amore, 1984). The main components of geothermal gases are carbon dioxide (CO<sub>2</sub>), hydrogen sulphide (H<sub>2</sub>S), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), nitrogen (N<sub>2</sub>) and ammonia (NH<sub>3</sub>) (Taran, 1986). Among these gases, H<sub>2</sub>S and CH<sub>4</sub> are produced by reduction of the original magmatic gases (sulphur dioxide (SO<sub>2</sub>) and CO<sub>2</sub>, respectively) at high temperature (above about 500°C) (Giggenbach, 1987). At lower temperatures, H<sub>2</sub>S and CO<sub>2</sub> concentrations seem to be controlled by mineral assemblage buffers (Nicholson, 1993). D’Amore and Nuti (1977) pointed out that geothermal NH<sub>3</sub> can be attributed to the thermal degradation of nitrogen-rich organic material, and geothermal H<sub>2</sub> due to water dissociation in high temperature and pressure conditions. Oxygen (O<sub>2</sub>), N<sub>2</sub> and argon (Ar) are likely to be of atmospheric origin (Giggenbach, 1976). However, on converging plate boundaries, a N<sub>2</sub> source may also be marine sediment organic matter (Giggenbach, 1992a).

Although the proportion of gas within steam (water vapour) geothermal discharge is small, the concentration of the gases together with the gas/steam and steam/water ratios can yield important information on subsurface conditions and on the behaviour of a field during exploitation. Therefore, the gas content of geothermal discharges (fumaroles and wells) has been used to obtain information on the source of the fluid and its temperature (Arnórsson et al., 2007).

### 4.2 Gas geothermometers

During exploration, chemical geothermometers provide rare and valuable windows into the deep system through which a geochemist sees. It is a challenge and, at the same time, an art for the geochemist to choose and interpret geothermometric data (Henley et al., 1984). Specifically for the application of gas geothermometers, it is very important to understand the thermodynamics of gas species which are thought to equilibrate in geothermal reservoirs (Powell, 2000).

The thermodynamic chemical equilibrium is the main and basic reference point in the majority of geochemical techniques which use the gas composition of geothermal fluids. This condition is set in time and space, and is only valid for a given period of time and in a given place of the reservoir. Neither the mass nor the energy in a natural open system, such as in a geothermal system, will ever be in full equilibrium. The period during which measurements are made and the reservoir parameters are calculated is very short compared to the normal lifespan of the entire system (D’Amore, 1991).

A thermodynamic equilibrium is always assumed despite the fact that each gas species is affected to a different degree by a kinetic response to the variation of thermal or redox conditions, both in the reservoir and during the ascent of the fluid towards the surface. It is the task of the geochemist, when interpreting data from any given geothermal field, to assess the validity of these assumptions and to justify the simplifications made (Arnórsson, 1991).

Semi-empirical and thermodynamic gas geothermometers are presented in this study. Gas ternary diagrams are used for geochemical evaluation. Equations for the application of these

geothermometers are presented in Table 1 in Appendix I. Description and equilibria of these geothermometers are presented below in a historical sequence.

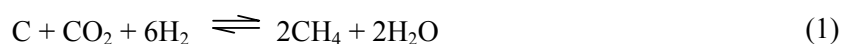
#### 4.2.1 Empirical and thermodynamic gas geothermometers

*D'Amore and Panichi (DAP) gas geothermometer (1980):*

D'Amore and Panichi developed a semi-empirical gas geothermometer based on the relative concentrations of H<sub>2</sub>S, H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> in 1980. They pointed out that a gas assemblage such as CO<sub>2</sub>-H<sub>2</sub>S-CH<sub>4</sub>-H<sub>2</sub>-N<sub>2</sub> is always present in or near thermal areas, and it is apparently possible to derive a suitable geochemical model of natural hydrothermal systems in which gas-water-rock equilibrium reactions occur. This model can be used in evaluating the deep geothermal temperatures using surface data on gas samples. It is intended to be applied to fumaroles, gas seeps and hot springs alike since it operates on simple gas ratios and an assumed value for the partial pressure of carbon dioxide ( $P_{CO_2}$ ). However, Powell (2000) has criticized the resulting temperature as being too strongly dependant on  $P_{CO_2}$ , which is arbitrary chosen. Therefore, it seems to work in some fields, but not in others.

The DAP geothermometer is based upon reactions between common carbon and sulphur bearing gases and reservoir minerals, and an empirical relationship for oxygen fugacity, as described below (D'Amore and Panichi, 1980):

a) Graphite, carbon dioxide and hydrogen react to form methane and H<sub>2</sub>O:



b) Anhydrite (CaSO<sub>4</sub>) and pyrite (FeS<sub>2</sub>), H<sub>2</sub>O and carbon dioxide react to form hydrogen sulphide, calcite, magnetite and oxygen:



c) The oxygen partial pressure  $P(O_2)$  is very low in the geothermal environment and is empirically related to temperature by:

$$\log P(O_2) = 8.2 - \frac{23643}{T} \quad (3)$$

d) The  $P_{CO_2}$  is related to its relative amount in the gas:

$$[CO_2] < 75 \text{ mol\%}, P_{CO_2} = 0.1 \text{ atm}; [CO_2] > 75 \text{ mol\%}, P_{CO_2} = 1 \text{ atm}; [CO_2] > 75 \text{ mol\%} \text{ and } [CH_4] > 2[H_2] \text{ and } [H_2S] > 2[H_2], P_{CO_2} = 10 \text{ atm}.$$

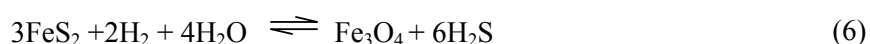
*Nehring and D'Amore (NDA) gas geothermometers (1984):*

Nehring and D'Amore developed two thermodynamic gas geothermometers as described below.

a) The H<sub>2</sub>/CO<sub>2</sub> geothermometer is based on the reaction of graphite and CO<sub>2</sub> controlling O<sub>2</sub> fugacity, and the reaction of water dissociation:



b) The H<sub>2</sub>S/CO<sub>2</sub> geothermometer is based on the reaction of graphite and CO<sub>2</sub> controlling O<sub>2</sub> fugacity (Reaction 4), and the reaction of pyrite-magnetite (Fe<sub>3</sub>O<sub>4</sub>) controlling sulphur (S) fugacity:





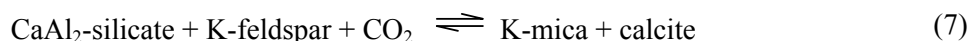
*Arnórsson and Gunnlaugsson gas geothermometers (1985):*

Arnórsson and Gunnlaugsson presented eight gas geothermometers in 1985. Three of them are based on the CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> concentrations for dilute and saline fluids, and two are based on gas ratios (CO<sub>2</sub>/H<sub>2</sub> and H<sub>2</sub>S/H<sub>2</sub>). Independent H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> geothermometer equations calibrated for dilute and saline fluids were presented. For both H<sub>2</sub>S and H<sub>2</sub> two curves were calibrated: a) one for all waters above 300°C and waters in between 200 and 300°C if chloride is above 500 ppm (saline); b) another for waters below 200°C and waters in between 200 and 300°C if chloride is below 500 ppm (dilute). Each geothermometer equation corresponds to equilibrium with a particular mineral assemblage. The pyrite-pyrrhotite-epidote-prehnite buffer is involved in controlling reservoir concentrations of these gases for dilute waters, whereas the pyrite-epidote-prehnite-magnetite buffer is involved with saline waters. At temperatures above 230°C, the epidote-prehnite-calcite-quartz assemblage was considered to buffer CO<sub>2</sub> (Arnórsson and Gunnlaugsson, 1985).

Calibration of these geothermometers was based on the observed concentration variations of CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> in well discharges with known reservoir temperature. These calibrations were based on the assumption of a single liquid phase in the reservoir at equilibrium with respect to the gases of the total well discharge composition. The type of data used to calibrate these geothermometers included hot-water wells, wet-steam wells with liquid enthalpy and wet-steam wells with “excess enthalpy”. These geothermometers are applied to systems with basaltic to acidic rocks and in sediments with similar composition.

*Giggenbach gas geothermometers (1991):*

Giggenbach developed three gas ratio geothermometers based on the ferrous to ferric ratio (Fe<sup>2+</sup>/Fe<sup>3+</sup>), which controls redox conditions in rock-fluid equilibria. Assuming that the argon concentration in geothermal fluid is constant, the ratio between this gas and H<sub>2</sub> or CO<sub>2</sub> does not change due to condensation processes on the way to the surface. Calibrations of the H<sub>2</sub>/Ar and CO<sub>2</sub>/Ar geothermometers are based on Ar concentrations corresponding with that of air-saturated water at 25°C. In addition, the CO<sub>2</sub> was considered to be buffered by the following reaction:



where  $P_{\text{CO}_2}$  as a function of temperature ( $T$ ) is:

$$\log P_{\text{CO}_2} = 0.0168T - 3.78 \quad (8)$$

The CH<sub>4</sub>/CO<sub>2</sub> geothermometer is based on the equilibrium reaction presented in Reaction 9. Among these gases, carbon monoxide (CO) is determined only rarely in geothermal vapour discharge due to its very low concentrations in geothermal systems with temperatures <280°C. Giggenbach pointed out that predicted subsurface temperatures above 300°C probably reflect slow rates of CH<sub>4</sub> equilibration and, thus, may indicate deeper temperature.

*Arnórsson et al. gas geothermometers (1998):*

Arnórsson et al. (1998) presented six thermodynamic gas geothermometers based on the assumption of equilibrium between aqueous concentration of CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub> and specific mineral buffers (Reactions 1, 6 and 11, Table 2 in Appendix I). The activity of the minerals involved in the equilibria are taken into account through a special term,  $k_o$ . The activities of clinozoisite and epidote were taken to be equal to 0.3 and 0.7, respectively, and unit activity was assumed for all other minerals and water. The compositions are representative of basaltic rocks. For other mineral compositions, another  $k_o$  must be selected.

The gas ratio geothermometers (CO<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>S/Ar and H<sub>2</sub>/Ar) were based on the assumption that N<sub>2</sub> and Ar concentrations in geothermal reservoir waters are equal to those in air-saturated water at 5°C, which is the annual mean temperature in Iceland.

### 4.2.2 Ternary diagrams

Ternary diagrams are used to spatially compare the geochemical characteristics of the gases or to identify their origin (Powell, 2010). In this study, only the N<sub>2</sub>-Ar-CO<sub>2</sub> ternary diagram will be discussed. This diagram can be used to distinguish the source of the gas as being magmatic, sedimentary, atmospheric or meteoric (Sepúlveda et al., 2007). In this diagram, CO<sub>2</sub> and N<sub>2</sub> are used as chemically inert tracers to their origins. The CO<sub>2</sub> is essentially of magmatic origin; N<sub>2</sub> and especially Ar are present in low concentrations in the magmatic gas (with a N<sub>2</sub>/Ar ratio of 800), but comprise major constituents of any contaminating atmospheric component. Saturated groundwater has a N<sub>2</sub>/Ar ratio of 38, and air has a higher ratio (N<sub>2</sub>/Ar ratio) of 84.

### 4.3 Equilibria associated with gases

Gas geothermometers may be based on assumptions of specific mineral-gas or gas-gas equilibria between gaseous species (Arnórsson et al., 2007). Minerals and solution species (especially dissolved gases) buffer the redox state of a hydrothermal system (Henley et al., 1984). Because of the dynamic nature of most hydrothermal alteration systems, the final equilibrium state, consisting of the complete conversion of an initially unstable to a thermodynamically stable fluid-rock system, is rarely attained (Giggenbach, 1981). But, at equilibrium, the composition of the fluid-mineral system is essentially determined by temperature and the initial chemical composition of the rock system and, therefore, can be expected to vary in different geothermal systems (Giggenbach, 1984).

The concentration of the gases in the steam phase may be controlled, or buffered, by mineral assemblages within the host rocks (Nicholson, 1993). The distribution of a mineral assemblage throughout a geothermal system reflects the stepwise conversion of thermodynamically unstable primary phases through a series of intermediate, metastable phases to a thermodynamically stable, secondary assemblage (Giggenbach, 1981). Therefore, these secondary minerals are results of the interaction of primary minerals with hydrothermal fluids in response to temperature, pressure or chemical changes in the surrounding environment (Lagat, 2007). The mineral-gas buffers that potentially could control the concentrations of H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> in the aquifer liquid (shown in Table 2 in Appendix I) will be evaluated in this study (Angcoy, 2010; González-Contreras, 2010). Symbols and formulae for the minerals are listed in Nomenclature.

## 5. METHODOLOGY

The primary data for this study were obtained from the liquid and gas discharges of nine wells from the Miravalles geothermal field (PGM-02, 07, 14, 17, 21, 29, 43, 44 and 49), six wells from the Pailas geothermal field (PGP-01, 03, 04, 08, 12 and 24), and from well PGB-01 and four fumaroles (RVMF01, RVNT05, RVMT08 and RVMT09) in the Borinquen area. PGM-02 and PGM-07 are classified as acid wells (aquifer pH <5), PGM-29 is a bicarbonate well (aquifer aqueous CO<sub>2</sub> above 20,000 ppm) and the other wells of Miravalles are neutral. The well samples were collected between 2007 and 2010, whereas the fumarole samples were collected between 2000 and 2006.

Data from three wells (RN-10, RN-12 and RN-19) and one fumarole (RN-G1) from Reykjanes geothermal field, SW-Iceland, and three wells (TG-01, TG-03 and TG-06) from Theistareykir geothermal field, northeast Iceland, were included in this study. Samples were collected between 2004 and 2009. Sampling techniques, analytical methods, handling of data and calculations are described in the following sections.

## 5.1 Sampling and physical-chemical analysis

Fumarole samples were collected at atmospheric conditions. Liquid and steam samples from both Costa Rican and Icelandic geothermal wells were collected in a Giggenbach bulb, which contained sodium hydroxide (NaOH), using a Webre-separator. Costa Rican liquid samples were collected at atmospheric conditions, whereas the steam samples were collected at separation pressure. In Icelandic samples, both liquid and steam phases were collected at separation pressure. Costa Rican samples were analysed in the Laboratory of Geochemistry at Miravalles geothermal field, whereas analyses of samples collected in the Icelandic fields were carried out by the geochemical laboratory at ÍSOR.

## 5.2 Data handling

Liquid and gas data were analysed, corrected and normalised to the same conditions, before the application of gas geothermometers; previously, their deep liquid compositions were computed. For reconstruction of the aquifer's initial composition, the total fluid from the wells was assumed to be representative of the deep brine in a liquid-dominated geothermal reservoir. Then, a single selected aquifer temperature was an approximation of the "real" temperature of the reservoir. These approximations and simplifications may introduce uncertainties in the results obtained by thermodynamic and geothermometer calculations.

### 5.2.1 Data quality analysis

Data from the chemical analysis of both the steam and liquid phases of a two-phase well should be checked before using them for further calculations. Two criteria were used, the oxygen content in the sample for the steam phase and the ionic balance in the liquid phase. It was assumed that no oxygen was present in the geothermal gas. Data that presented less than one volume percent of oxygen in head space gas and with a negative or positive ionic balance of less than three percent were selected for further consideration. The detection of the presence of oxygen indicated air contamination. In this case, the analyses could be corrected by subtracting the atmospheric component. The composition of air is given in Table 1.

TABLE 1: Air composition by volume percentage

Name	Symbol	Percent by volume (%)
Nitrogen	N <sub>2</sub>	78.084
Oxygen	O <sub>2</sub>	20.9476
Argon	Ar	0.934
Carbon dioxide	CO <sub>2</sub>	0.0314
Methane	CH <sub>4</sub>	0.0002
Helium	He	0.000524
Hydrogen	H <sub>2</sub>	0.00005

Source: Lide, 1997

The ratio of a gas compound and oxygen concentrations in air can be applied for correcting the equivalent amount of oxygen incorporated in the sample by air contamination. These values can be taken from Table 1. The ratio of a gas compound  $i$  ( $r_i^a$ ) is estimated with the concentration of the gas in air ( $m_i^a$ ) and the content of oxygen in air ( $m_{O_2}^a$ ) according to Equation 10:

$$r_i^a = \frac{m_i^a}{m_{O_2}^a} \quad (10)$$

The concentration of the gas compound in the geothermal gas is calculated by subtracting the equivalent amount of oxygen ( $r_i^a m_{O_2}^s$ ) as presented in Equation 11:

$$m_i^g = m_i^s - r_i^a m_{O_2}^s \quad (11)$$

### 5.2.2 Selection of aquifer reference temperature

To compute the deep fluid composition and to evaluate the gas geothermometers, the aquifer reference temperature was selected as described below. For the liquid phase, three solute geothermometers were calculated: sodium-potassium (Na-K) Fournier geothermometer, sodium-potassium-calcium (Na-K-Ca) geothermometer and quartz geothermometer (Arnórsson, 2000). Sampling of the liquid phase was carried out in duplicate and the average of the concentrations of sodium, potassium, calcium and silica was used for the calculation of the geothermometers. Three samples collected between 2007 and 2010 for each well were computed for the average of each geothermometer. Then, a global average was estimated for the three geothermometers that were applied to all the samples. Additionally, the temperature below the boiling point in the liquid phase was measured for each well by the Laboratory of Thermohydraulic Measurements at Miravalles geothermal field. According to this measured temperature and the global average temperature estimated by geothermometers, an aquifer reference temperature ( $T_R$ ) was defined for each well.

The difference between the three solute geothermometers was between 1 and 23°C for the Miravalles wells, between 24 and 49°C for the Pailas wells, and between 13 and 21°C for the Borinquen well. The difference in temperature between that predicted by solute geothermometers and the downhole measured temperatures for five wells in Miravalles geothermal field (PGM-17, 21, 29, 44 and 49) was small (from 2 to 8°C). Therefore, for these wells the temperature of the liquid phase just below the boiling level was defined as the reference temperature. For the other Miravalles wells, the global average temperature estimated by three solute geothermometers applied to three samples was defined as the reference temperature for the wells.

For the Pailas and Borinquen geothermal fields, the average of the temperature below the boiling point and the quartz geothermometer was defined as the reference temperature. The Na/K and Na/K/Ca geothermometers predicted higher temperatures than those observed with a quartz geothermometer and downhole measurements. Na and K exchange reactions between alkali feldspars and solutions occur very slowly at temperatures below about 300°C; accordingly, the Na/K geothermometer estimates higher temperature in deeper parts of the system where waters reside for relatively long periods of time (Fournier, 1991). The Na/K/Ca geothermometer is sensitive to the partial pressure of CO<sub>2</sub>, so if waters initially have high CO<sub>2</sub> and Ca concentrations, a high predicted subsurface temperature may result due to rapid deposition of calcium carbonate during the ascent from the aquifer to the surface (Fournier and Truesdell, 1973). The quartz geothermometer, compared to the Na/K geothermometer, predicted lower subsurface temperature, because attainment to a new water rock chemical equilibrium in shallower reservoirs where waters reside for short periods of time is faster for quartz than Na/K (Giggenbach, 1988; Fournier, 1991).

In Table 2, the subsurface temperature estimated by solute geothermometers and downhole measurements, and the reference temperatures for Miravalles, Pailas and Borinquen geothermal wells are shown.

### 5.2.3 Gas data correction to atmospheric pressure

Gas samples were collected at separation pressure ( $P_s$ ) of the Webre-separator, whereas liquid samples were collected at atmospheric pressure ( $P_a$ ). In order to compute the deep liquid compositions, it was necessary to collect the steam and liquid analyses using the same conditions, specifically at the same steam fraction. Thus, the gas composition was corrected to atmospheric pressure.

The reference temperature ( $T_R$ ) was used for estimating the enthalpy of the saturated liquid ( $h^{dl}$ ) in the reservoir. The enthalpy of the saturated liquid ( $h^w$ ) and steam ( $h^s$ ) at sampling pressure ( $P_s$ ) were obtained from steam tables. Then, the steam fraction at sampling pressure ( $X_{P_s}$ ) was calculated using Equation 12:

$$X = \frac{h^{dl} - h^w}{h^s - h^w} \quad (12)$$

The steam fraction at atmospheric pressure ( $X_{Pa}$ ) should be calculated using Equation 12 using  $h^w$  and  $h^s$  at atmospheric pressure. Then, the concentration of each gas at atmospheric pressure ( $C_{Pa}$ ) is calculated with the ratio of the steam fractions at sampling pressure and atmospheric pressure. To find the concentration of the gas collected at sampling pressure ( $C_{Ps}$ ), Equation 13 is applied:

$$C_{Pa} = \frac{X_{Ps}}{X_{Pa}} C_{Ps} \quad (13)$$

Data corrected for atmospheric contamination and at atmospheric conditions (1 bar-a and 100°C) are presented in Table 3 in Appendix I.

TABLE 2: Temperature estimated by solute geothermometers, downhole and reference temperatures for Miravalles, Pailas and Borinquen geothermal wells

Well	Na-K Fournier geothermometer (°C)	Na-K-Ca geothermometer (°C)	Quartz geothermometer (°C)	Global average s.g. T (°C)	Down-hole temp. (°C)	Reference temperature (°C)
PGM-02	237	241	236	238	NA	<b>238</b>
PGM-07	238	242	244	241	245	<b>241</b>
PGM-14	237	234	239	237	230	<b>237</b>
PGM-17	233	232	231	232	235	<b>235</b>
PGM-21	232	228	226	229	233	<b>233</b>
PGM-29	207	214	230	217	232	<b>232</b>
PGM-43	235	232	229	232	232	<b>232</b>
PGM-44	234	228	224	228	230	<b>230</b>
PGM-49	228	226	224	226	220	<b>220</b>
PGP-01	285	268	241	265	245	<b>243</b>
PGP-03	284	269	243	265	249	<b>246</b>
PGP-04	281	264	232	259	232	<b>225</b>
PGP-08	277	264	240	260	232	<b>235</b>
PGP-12	288	272	243	268	245	<b>244</b>
PGP-24	284	271	247	267	NA	<b>247</b>
PGB-01	263	254	241	252	248	<b>241</b>

PGM: Miravalles well; PGP: Las Pailas well; PGB: Borinquen well; NA: no dynamic temperature and pressure profiles; s.g.: solute geothermometer; T: temperature.

### 5.3 Evaluation of gas geothermometers

The application of gas geothermometers is based on the following assumption: the total fluid from the wells (gas, steam and residual brine) is representative of the deep brine in the geothermal reservoir; in other words, there is only one phase at depth in a liquid-dominated reservoir. The subsurface temperature of the sites was estimated by the application of 21 gas geothermometers presented in Table 1 in Appendix I; their results are presented in Table 4 in Appendix I. An explicit equation was derived for Giggenbach's (1991) gas ratio geothermometer 13 ( $\text{CO}_2/\text{Ar}$ ).

### 5.4 Calculation of mineral equilibria buffers

The analytical data of samples collected at wellheads were used to compute the deep aquifer liquid composition with the aid of the speciation programme WATCH (Arnórsson et al., 1982), version 2.4

(Bjarnason, 2010). For Icelandic geothermal fluids, adiabatic boiling between aquifer and wellhead was assumed to compute their steam composition at atmospheric conditions (1 bar-a and 100°C). The chemical composition and partial pressure of gases were computed at the reference temperature defined for each well. The partial pressure of H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> calculated in the deep geothermal liquid was plotted as a function of temperature in respective gas mineral buffer equilibria.

Solubility constants (*K*) for mineral buffers were calculated with the aid of the thermodynamic programme SUPCRT92 (Johnson et al., 1992). The computed partial pressure of H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> that could potentially be controlled by mineral-gas reactions are listed in Table 5 in Appendix I. Unit activity was assumed for all minerals (anhydrite, calcite, hematite, magnetite, pyrite, pyrrhotite, quartz, and wollastonite) except for epidote and prehnite solid solutions. Observed compositions of epidote and prehnite from Miravalles geothermal system ranged between 0.18 and 0.21 for *X<sub>ps</sub>* in epidote and 0.04 and 0.24 for *X<sub>pre</sub>* in prehnite (where *X<sub>pre</sub>* is = Al/(Al + Fe) in prehnite solid solution) (Milodowski et al., 1989; cited by Bird and Spielier, 2004). Consequently, a mean activity of 0.25 was used for clinozoisite, 0.75 for epidote and 0.86 for prehnite. For a CO<sub>2</sub> mineral buffer, minimum (clinozoisite: 0.04 and prehnite: 0.76) and maximum (clinozoisite: 0.25 and prehnite: 0.86) activities were modelled. The computed equilibrium constants of the mineral assemblage equilibria are presented in Table 6 in Appendix I.

## 6. RESULTS AND DISCUSSIONS

Identification of the origin of gases that compose a sample allows distinguishing the contributions from different sources. A ternary diagram is a practical tool for geochemists. Alteration mineralogy and fluid composition are also important for identifying the redox state of geothermal systems. Since mineral assemblages differ from an oxidised to a reduced system, secondary minerals are helpful in mineral-gas equilibria assessment. This evaluation is based on the concept that the local equilibrium of a subsystem is representative of large and open geothermal systems. Therefore, the local equilibrium of fluids with hydrothermal minerals within a subsystem is assumed to represent the overall condition of the geothermal system. Dissolved gases within a deep reservoir are assumed to be controlled by one or several assemblages. Partial pressures of most of these gases are fixed by temperature-dependent mineral solution equilibria. Gas geothermometers are based on temperature equations. Thus, interpretation of subsurface temperature predicted by gas geothermometers should be carried out considering mineral-gas or gas-gas equilibria.

### 6.1 Origin of gases

The ternary N<sub>2</sub>-CO<sub>2</sub>-Ar diagram presented in Figure 4 allows the identification of the sources of geothermal gases. Possible sources include magma or sediments, atmosphere and meteoric water. Relative contents of CO<sub>2</sub>, 100 times of N<sub>2</sub> and 10000 of Ar are plotted in the diagram. Among these gases, CO<sub>2</sub> is the only one essentially of magmatic origin, whereas N<sub>2</sub> and Ar originate mainly from atmospheric sources (air and air saturated water: Giggenbach, 1987). Argon as a noble gas is unlikely to be changed by any chemical process lowering its original concentrations. Its solubility in water, at elevated temperature, is similar to that of N<sub>2</sub> (Giggenbach, 1997). The atmospheric source can be identified based on the N<sub>2</sub>/Ar ratio; air saturated groundwater (ASW) has N<sub>2</sub>/Ar molar ratio of 38, while free air has a N<sub>2</sub>/Ar ratio of 84 (Giggenbach, 1991). The N<sub>2</sub>/Ar ratios of Theistareykir and Reykjanes gases (mean of 50) are slightly higher than that of ASW. These ratios indicate that the gases are essentially of meteoric origin. The N<sub>2</sub>/Ar ratio of fumarole RVMT08 (536) is close to that of magmatic origin (800). Pailas (N<sub>2</sub>/Ar ratios between 69 and 103) and Borinquen (88) have great amounts of N<sub>2</sub>, because these wells were pressurised with air before being opened for evaluation. Therefore, in these cases, the origin of N<sub>2</sub> is mainly atmospheric.

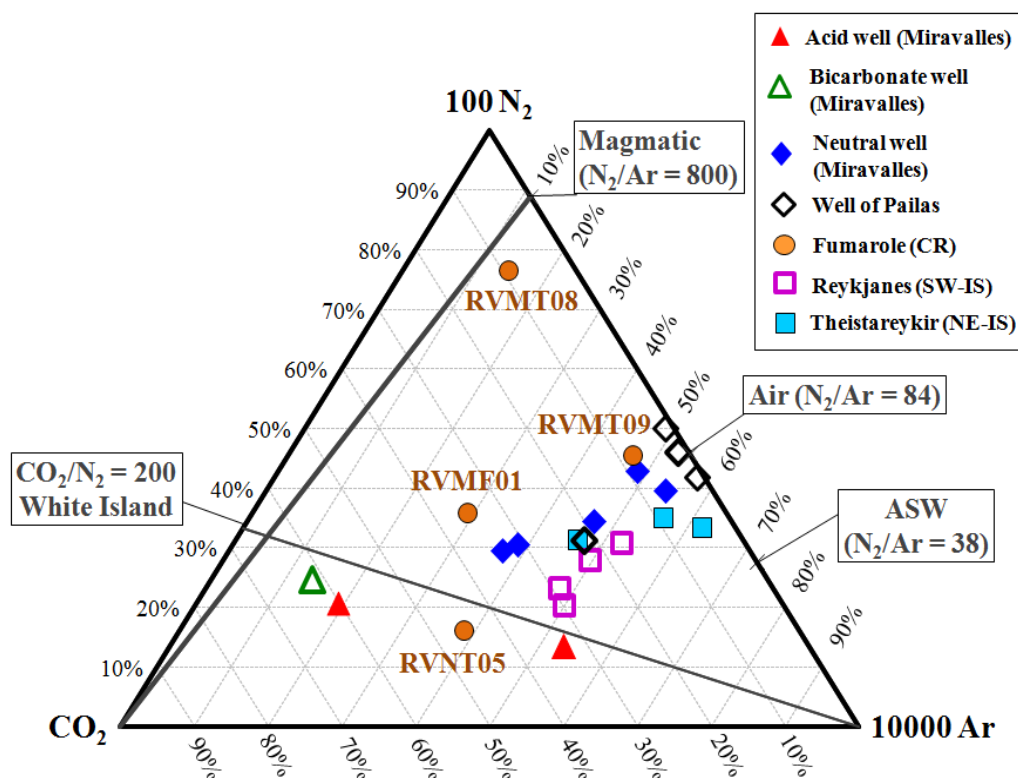


FIGURE 4: Ternary diagram of N<sub>2</sub>-CO<sub>2</sub>-Ar for Costa Rican (CR) (Miravalles, Pailas and Borinquen) and Icelandic (Reykjanes and Theistareykir) geothermal fluids

An increase in N<sub>2</sub>/Ar ratio in andesitic gases is likely due to thermal decomposition of organic material (Giggenbach, 1997). In convergent boundary plates, the N<sub>2</sub>/Ar ratio is higher than that of basaltic gases due to the addition of nitrogen from subducted sediments (Giggenbach, 1992b). The neutral wells of Miravalles present higher N<sub>2</sub>/Ar ratios (mean of 77, Table 3 in Appendix I) than that of Icelandic wells (mean N<sub>2</sub>/Ar of 50).

Giggenbach (1987) found that most of the gas samples from the volcanic system of White Island, which is fed by a magmatic source, had a CO<sub>2</sub>/N<sub>2</sub> ratio of 200. This ratio was plotted where the N<sub>2</sub>/Ar ratio (near the 800 line) and the Ar corner line intersect. Gases from fumarole RVNT05, acid wells and the bicarbonate well are close to the line that connects the ratio of White Island and the Ar corner. The CO<sub>2</sub>/N<sub>2</sub> ratios of these sites are between 222 and 283. This may indicate that gas compositions of these wells are affected by a magmatic gas component.

The other fumaroles (RVMF01 and RVMT09), some neutral wells of Miravalles and wells of Reykjanes and Theistareykir aligned between the ASW N<sub>2</sub>/Ar ratio point and the White Island CO<sub>2</sub>/N<sub>2</sub> ratio point. The N<sub>2</sub>/Ar ratios of these sites are between 41 and 59. This may indicate that gases at these sites are mixtures of magmatic and meteoric origins.

## 6.2 Hydrothermal alteration and equilibria associated with gases

The chemistry of the fluids, (liquid and gases) collected at the surface, and of secondary minerals provides information about the effects of hydrothermal fluid interaction with the primary rock matrix. Fluid discharges represent a moment in time, whereas hydrothermal minerals represent a product of water-rock interaction formed over a period of time (Karingithi et al., 2010). Surface fluid composition was recalculated with a speciation programme in order to obtain its deep composition. In this way, this information can be related to mineral assemblages within a geothermal system. Application of thermodynamics is an attempt to model local mineral equilibria that could potentially

control the gas partial pressures in the reservoir. Since gas geothermometers are based on mineral-gas assemblages or gas-gas reactions, the understanding of the relationship between secondary minerals and deep gas composition is important in order to evaluate gas geothermometers. The equilibrium curves of the mineral assemblages that could potentially fix the concentrations of the reactive gases H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> and Fischer-Tropsch gas-gas reaction are presented in Figure 5.

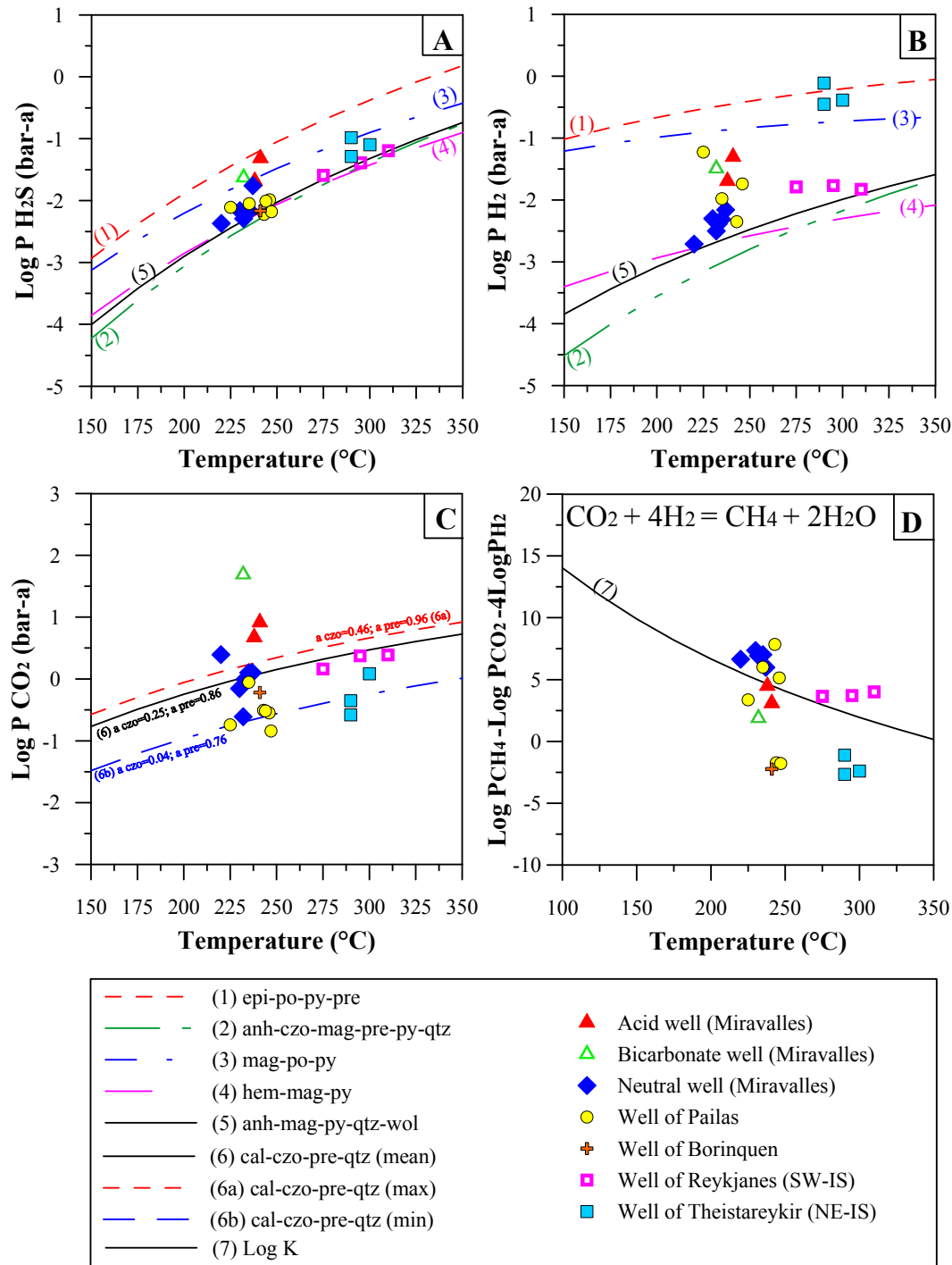


FIGURE 5: Partial pressure of H<sub>2</sub>S (A), H<sub>2</sub> (B) and CO<sub>2</sub> (C) of Costa Rican (Miravalles, Pailas and Borinquen) and Icelandic (Reykjanes and Theistareykir) geothermal fluids as a function of temperature for theoretical mineral buffer equilibria, and equilibrium with respect to CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub> (D) as a function of temperature in geothermal reservoir fluids



The secondary minerals such as pyrite, calcite, quartz, epidote and anhydrite are found in wells of Miravalles (Vega et al., 2005) and Pailas geothermal systems (Mora and Herrera, 2002). Secondary minerals in active geothermal systems in Iceland have been identified. Pyrite, chlorite, prehnite, epidote, wollastonite, albite and K-feldspar are frequently identified as secondary minerals (Franzson et al., 2002). Calcite is found at all temperatures, and chalcedony and quartz below and above 180°C, respectively (Stefánsson and Arnórsson, 2002). In the geothermal seawater systems on Reykjanes Peninsula, pyrrhotite is absent, whereas anhydrite and magnetite are abundant (Sveinbjörnsdóttir, 1992). Pyrite and pyrrhotite are found in geothermal systems associated with dilute fluids such as those at Theistareykir (Gudmundsson and Arnórsson, 2004) but there anhydrite is absent. Consequently, geothermal systems with dilute fluids have more reduced mineral assemblages, while in saline systems the minerals are more oxidised.

Figure 5 shows the mineral assemblage buffers for H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub>, and the Fischer-Tropsch equilibria. Figures 5A and 5B show the mineral assemblage equilibria that could potentially fix partial pressures of both aquifer H<sub>2</sub>S and H<sub>2</sub> as a function of temperature. The most reduced mineral assemblages are represented by the uppermost lines, and the most oxidised buffers with the more negative values. Two assemblage buffers (1 and 3) contain pyrrhotite, which is a secondary mineral characteristic of dilute and reduced geothermal systems (Stefánsson and Arnórsson, 2002). It is important to emphasise that the mineral assemblages and buffers both have a partial pressure of H<sub>2</sub>S and H<sub>2</sub> (Table 2 in Appendix I). A discussion about the results of each gas will be carried out separately below.

Aquifer H<sub>2</sub>S partial pressures in saline (approximately 18,000 and 20,000 ppm of Cl) fluids of Reykjanes match well the equilibrium pressures of three mineral buffers (2, 4 and 5 in Figure 5A). Among these three buffers, Stefánsson and Arnórsson (2002) suggested that buffer 2 (anh-czo-mag-pre-py-qtz) controls the H<sub>2</sub>S partial pressure above 200°C for saline fluids, and for the dilute fluids, buffer 1 (epi-po-py-pre) is in control. According to the results, observed aquifer H<sub>2</sub>S partial pressure in the dilute fluids of Theistareykir match closely the equilibrium pressures of buffer 3 (mag-po-py). Equilibrium pressures of the three buffers that control saline fluids correspond to the aquifer H<sub>2</sub>S partial pressure of the Pailas and Borinquen wells as well as the majority of Miravalles wells except for the acid and bicarbonate wells. Concerning the acid fluids, Chavarría (2003) concluded that they are not in equilibrium with the alteration mineralogy, probably due to the short time of residence. Pyrrhotite was identified in one acid well PGM-02; in the other acid well (PGM-07) and the bicarbonate well (PGM-29), these analyses have not yet been carried out (Vega, personal communication on October 5<sup>th</sup>, 2010). Therefore, aquifer partial pressure of H<sub>2</sub>S in PGM-02 seems to be controlled by the more reducing buffers (1 and 3).

The hydrogen concentration in dilute and reduced geothermal systems is higher (ranges between 7 and 23 mol% dry gas for Theistareykir wells) than in more oxidised systems such as Reykjanes (<1 mol% dry gas). The aquifer H<sub>2</sub> partial pressure of Theistareykir matches closely to equilibrium pressures of buffer 1 in Figure 5B. The results indicate that the mineral epi-po-py-pre buffer controls the partial pressure of H<sub>2</sub> in the dilute (<100 ppm Cl) Theistareykir geothermal system, and also the H<sub>2</sub> aqueous concentration at high temperature (from 290 to 300°C). On the other hand, H<sub>2</sub> partial pressure of the Reykjanes fluid matches closely equilibrium values of two buffers (2 and 5). Stefánsson and Arnórsson (2002) concluded that buffer 2 (anh-czo-mag-pre-py-qtz) controls H<sub>2</sub> aquifer concentrations for saline geothermal system of basaltic composition. Buffer 5 (anh-mag-py-qtz-wol) is likely to control H<sub>2</sub> partial pressure for Reykjanes well fluids as these secondary minerals are common in the geothermal system (Franzson et al., 2002).

In andesitic geothermal systems, the partial pressure of H<sub>2</sub> in the aquifer of most of the neutral wells of Miravalles and one of Pailas (PGP-01) approaches closely the equilibrium pressures of two buffers (4 and 5 in Figure 5B). However, wollastonite was not found in these geothermal systems, so anh-mag-py-qtz-wol buffers are uncommon. Aquifer H<sub>2</sub> of acid and bicarbonate wells of Miravalles, and other wells of Pailas and Borinquen is higher than that corresponding to equilibrium with mineral

assemblages 4 or 5. This observation is consistent with the H<sub>2</sub>S partial pressure calculated for the acid fluids, which are not in equilibrium with alteration mineralogy (Chavarría, 2003).

Anhydrite was reported in the Miravalles and Pailas geothermal systems (Vega et al., 2005; Mora and Herrera, 2002). The presence of this mineral reflects more oxidising conditions in these geothermal systems (Browne, 1978). Therefore, aquifer partial pressures of more reduced gases such as H<sub>2</sub>S and H<sub>2</sub> are lower in these systems compared to geothermal systems which lack this mineral. Aquifer partial pressures of Theistareykir geothermal fluids are between 0.05 and 0.1 bar of H<sub>2</sub>S, and between 0.3 and 0.8 bar of H<sub>2</sub> (Table 3 in Appendix I), whereas, the aquifer partial pressure of these gases in the Costa Rican geothermal systems is below 0.05 bar of H<sub>2</sub>S and H<sub>2</sub>. Aquifer partial pressure of these gases at Reykjanes geothermal fluids are similar (<0.06 bar of H<sub>2</sub>S and <0.02 bar of H<sub>2</sub>). In addition, high aquifer partial pressure of H<sub>2</sub> in the dilute fluids of the Theistareykir geothermal system is consistent with the presence of pyrrhotite, which reflects more reduced conditions.

The aquifer CO<sub>2</sub> partial pressures of Reykjanes saline fluids, PGP-01, PGB-01 and most of the neutral fluids of Miravalles match closely the average of the mineral assemblage buffer in Figure 5C. Partial pressures of CO<sub>2</sub> in fluids of two wells at Theistareykir (TG-01 and TG-03) are significantly lower than equilibrium pressures. The average composition of prehnite ( $X_{Al,pre}$ ) for Reykjanes is from 0.41 to 0.87, calculated from  $X_{Fe,pre}$  (Freedman et al., 2009). This value is close to the Miravalles average mineral composition and, therefore, the equilibrium pressures are expected to be close to that of Miravalles. Aquifer partial pressure of CO<sub>2</sub> of most of the Pailas fluids is between equilibrium pressures calculated for the minimum and average mineral composition of clinozoisite and prehnite in the mineral equilibrium. Exceptions include Miravalles bicarbonate and acid fluids, in which an elevated levels of CO<sub>2</sub> were observed. The cause of the high aquifer CO<sub>2</sub> partial pressure may be due to acid reservoir fluids derived from volcanic fluid being incompletely neutralised by reaction with feldspars, micas and iron minerals (Truesdell, 1991). These types of geothermal fluids are associated with immature and recently andesitic volcanoes such as Miravalles.

Equilibrium between CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> in the aquifer fluid is presented in Figure 5D. These gases are involved in the gas-gas Fischer-Tropsch reaction. Partial pressures of these gases of some neutral fluids of Miravalles match closely the equilibrium values. However, most of the Pailas, Borinquen, acid and bicarbonate fluids of Miravalles as well as the Icelandic geothermal fluids do not match the gas-gas equilibrium pressures. The same conclusion was reached by Stefánsson and Arnórsson (2002). Giggenbach (1987) showed that the CH<sub>4</sub>/CO<sub>2</sub> ratio did not equilibrate to low temperature (~300°C) and low pressures (~100 bars). The response of CH<sub>4</sub> to variations in both temperature and redox conditions could be expected to be somewhat slower than that of H<sub>2</sub>. Arnórsson and Gunnlaugsson (1985) pointed out that the reduction of CO<sub>2</sub> is very slow and the concentration of CH<sub>4</sub> is insufficient to attain overall equilibrium. According to the observed results, this gas-gas equilibrium is not attained at lower temperature (<310°C) in the geothermal systems evaluated in this study.

### 6.3 Gas geothermometers

Decreases in temperature and pressure over the uppermost approximately two kilometres of geothermal systems affect relative H<sub>2</sub>S, H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and Ar contents only a little; gas samples, taken from natural features during the exploration stages of a geothermal system for power production, are able to provide reliable information on conditions at depth (Giggenbach, 1992b). Therefore, gas geothermometers can be used as reliable indicators of subsurface temperature.

The evaluation of mineral assemblage equilibria carried out above indicates that some mineral buffers are involved in controlling partial pressures in the reservoir. The mineral assemblage buffer which constrains the H<sub>2</sub>S and H<sub>2</sub> partial pressures depends on the secondary mineral composition and the fluid salinity of the geothermal systems. A summary of this evaluation is presented in Table 3 below.

The same mineral assemblage (cal-czo-pre-qtz) buffer controls CO<sub>2</sub> partial pressure in both the basaltic and andesitic high-temperature geothermal systems evaluated in this study.

TABLE 3: Mineral assemblage buffers evaluated for Icelandic and Costa Rican geothermal systems

Rock composition	Country	Geothermal area	Redox state of the system	Salinity of deep fluid (ppm Cl)	Mineral assemblage buffer for controlling partial pressure of H <sub>2</sub> S and H <sub>2</sub>
Basaltic	Iceland	Theistareykir	Reducing	Dilute (<500)	epi-po-py-pre mag-po-py
Basaltic	Iceland	Reykjanes	Oxidizing	Saline (~20,000)	anh-czo-mag-pre-py-qtz
Andesitic	Costa Rica	Miravalles (neutral fluids)	Oxidizing	Saline (~3,000)	hem-mag-py
Andesitic	Costa Rica	Pailas and Borinquen	Oxidizing	Saline (~5,000)	anh-mag-py-qtz-wol

### 6.3.1 Gas geothermometers and mineral buffers

Single gas geothermometers developed by Arnórsson and Gunnlaugsson in 1985 and Arnórsson et al. in 1998 are based on mineral assemblage buffers that could potentially control the respective gas concentration in the reservoir. These geothermometers are the H<sub>2</sub>S (5, 6 and 17, Table 1 in Appendix I), H<sub>2</sub> (7, 8 and 18) and CO<sub>2</sub> (15 and 16). Among them, geothermometers 6 and 8 are calibrated for dilute waters (<500 ppm Cl) and geothermometers 15, 17 and 18 are derived from mineral assemblage buffers found in reducing state systems such as Krafla and Theistareykir in Iceland. In these mineral assemblages, pyrrhotite is a commonly found. Therefore, the application of these geothermometers in more oxidised systems, such as Reykjanes and the Costa Rican geothermal areas, predicts too low subsurface temperature. Geothermometers (17 and 18) calibrated for reducing state geothermal systems predict lower temperature than those calibrated for more oxidizing systems (geothermometers 5 and 7). The underestimated subsurface temperature by H<sub>2</sub>S geothermometers ranges from 51 to 74°C (Table 4 in Appendix I) for Miravalles neutral wells (PGM-14, 17, 21 and 44) and from 3 to 20°C for Reykjanes wells. This trend is similar for H<sub>2</sub> geothermometers (ranges from 25 to 136°C for Miravalles neutral wells, and from 11 to 19°C for Reykjanes wells). Pyrrhotite was not found in either Reykjanes or neutral Miravalles geothermal areas. Consequently, in these areas, geothermometers 17 and 18 are not appropriate.

On the other hand, geothermometers 6 and 8, developed for dilute fluids, and geothermometers 15, 17 and 18 are appropriate for Theistareykir wells due to its chemical composition and similar secondary minerals to Krafla. However, aquifer H<sub>2</sub>S and CO<sub>2</sub> partial pressures in Theistareykir wells are lower than those of epi-po-py-pre and cal-czo-pre-qtz assemblage buffers, respectively, on which the calibration of these geothermometers was based. Only H<sub>2</sub> partial pressures approached equilibrium closely with this buffer (1 in Figure 5B). For Theistareykir fluids, the difference in temperature between those predicted by H<sub>2</sub> geothermometer 7 (for saline fluids) and reference temperature ranged between 7 and 10°C (Table 4 in Appendix I), whereas H<sub>2</sub> geothermometer 18 predicted variable temperature from 3 to 31°C. Despite the estimated larger difference in temperature by the latter, it should be more appropriate to use this geothermometer for Theistareykir if all the minerals involved in the buffer were found in this area.

Aquifer partial pressures of H<sub>2</sub>S and H<sub>2</sub> in Reykjanes and Miravalles neutral fluids are controlled by any of the three buffers presented in Table 3. H<sub>2</sub>S and H<sub>2</sub> equilibrium pressure values of this set of mineral buffers are similar (Figures 5A and 5B). Therefore, no matter which of these mineral assemblage buffers is in control, the gas partial pressure will not significantly change the aqueous concentrations at equilibrium. The difference in the subsurface temperature compared to the reference temperature predicted by H<sub>2</sub>S geothermometer 5 ranged from 5 to 13°C for Miravalles neutral wells, and from 12 to 28°C for Reykjanes wells, whereas H<sub>2</sub> geothermometer 7 ranged from 5 to 25°C for Miravalles neutral wells, and from 7 to 47°C for Reykjanes wells.

According to Arnórsson and Gunnlaugsson (1985), the CO<sub>2</sub> geothermometer 4 was calibrated for all waters. This means that it is suitable for both dilute and saline geothermal fluids, and in basaltic to acidic rocks and in sediments with similar composition. They suggested that CO<sub>2</sub> was buffered by the cal-czo-pre-qtz assemblage buffer (Figure 5C). For aquifer CO<sub>2</sub> partial pressure of wells that is close to the equilibrium pressures of this buffer, this geothermometer predicts a smaller difference in temperature than in those wells whose partial pressures are much higher or lower. The difference in the subsurface temperature compared to the reference temperature for the majority of the neutral wells at Miravalles is between 1 and 10°C. This difference is higher for Icelandic wells (from 32 to 127°C). The difference in predicted temperature for Theistareykir (from 58 to 127°C) is higher than that for Reykjanes (from 32 to 46°C). These results are consistent with the CO<sub>2</sub> partial pressure of Theistareykir observed in the cal-czo-pre-qtz assemblage buffer. This partial pressure is lower than that of equilibrium, and therefore, the predicted subsurface temperature is lower than the reference temperature.

CO<sub>2</sub> geothermometer 16 of Arnórsson et al. (1998) is appropriate for Miravalles neutral wells and Reykjanes wells, because this geothermometer was calibrated with an activity of 0.7 for epidote solid solution. This value is close to that found at Miravalles (0.75) (Milodowski et al., 1989; cited by Bird and Spielier, 2004). In addition to epidote, calcite, prehnite and quartz have been found at both Miravalles and Reykjanes geothermal systems. The small difference in epidote activity (0.05), between that found at Miravalles and Reykjanes, reflects a small difference in temperature between the predicted and the referenced temperatures. The difference in subsurface temperature compared to the reference temperature for Reykjanes wells ranged from 2 to 9°C, whereas for the Miravalles neutral wells, it varied from 20 to 46°C except for two wells (PGM-43 and PGM-49). PGM-49 presented a small amount of CO<sub>2</sub> in excess and in PGM-43 the partial pressure was less than that of equilibrium. This disequilibrium of CO<sub>2</sub> in these two wells reflects a wide variation in the predicted subsurface temperature. The Theistareykir predicted subsurface temperature by CO<sub>2</sub> geothermometer 15 showed a similar trend as PGM-43. Although CO<sub>2</sub> geothermometer 15 is calibrated for dilute geothermal systems, this geothermometer underestimated by almost 100°C when compared to the reference temperature due to the observed lack of equilibrium with the buffer (Figure 5C).

Anhydrite was found in neutral wells at Miravalles. According to Chavarría (2003), this mineral is more common in acid wells than in neutral ones. It is slightly more abundant in acid well PGM-07 than in neutral well PGM-44. He also concluded that acid fluids are not in equilibrium with the alteration mineralogy. However, according to Vega (personal communication on October 5<sup>th</sup>, 2010), pyrrhotite was identified in acid well PGM-02. For the other acid well PGM-07 and bicarbonate well PGM-29, analyses for the identification of pyrrhotite have not been carried out yet. Therefore, two possible explanations can be derived from these statements for acid and bicarbonate wells at Miravalles. On one hand, an excess of aquifer H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> partial pressures observed in acid wells (Figure 5) can be attributed to the lack of equilibrium in these fluids due to the contribution of gases from recent active volcanoes (Truesdell, 1991). On the other hand, aquifer H<sub>2</sub>S partial pressure in acid and bicarbonate wells may be potentially controlled by two mineral assemblage buffers, either epi-po-py-pre (1) or mag-po-py (3). However, H<sub>2</sub>S geothermometers 6 and 17 calibrated for dilute and reducing systems underestimated subsurface temperature compared to the reference temperatures, ranging between 35 and 40°C. This difference in temperature is smaller for the other acid well PGM-07 (from 12 to 20°C) and bicarbonate well PGM-29 (from 21 to 25°C). Anhydrite was found in these two wells, but pyrrhohite has not been identified yet. It is important to identify which of these minerals is present in the aquifers of these wells. With this information, a conclusion about these wells could be achieved.

### 6.3.2 Gas geothermometers and gas-gas equilibria

Geothermometer 14 ( $\text{CH}_4/\text{CO}_2$ ), introduced by Giggenbach (1991), overestimated the subsurface temperature by more than  $100^\circ\text{C}$  at most of the sites (Table 4 in Appendix I). According to the author, these high temperatures indicate temperature in the deeper parts of the geothermal system, where equilibria of the ferrous-ferric buffer and the  $\text{H}_2\text{S}/\text{SO}_2$  magmatic vapours approach. Besides, equilibration of Reaction 9 at temperatures below  $300^\circ\text{C}$  is very slow (Giggenbach, 1991). Therefore, this geothermometer is applicable for high-temperature volcanic systems or areas where magmatic vapours reach the surface. For geothermal systems such as those presented in this study (reservoir temperature  $\leq 300^\circ\text{C}$ ), this geothermometer is not applicable. In addition,  $\text{CH}_4$  is a decomposition product of organic matter. Thus, on convergent plate boundaries or sedimentary reservoirs, the concentration of this gas is higher than that on divergent plate boundaries. Methane concentrations in Costa Rican geothermal fluids range between 0.01 mmol/kg and 36 mmol/kg steam, whereas in Icelandic fluids, it is less than 0.03 mmol/kg steam (Table 3 in Appendix I).

### 6.3.3 Gas ratio geothermometers

Gas ratios have the major advantage of being dimensionless and, therefore, being independent of absolute concentrations (Giggenbach, 1992a). Gas ratio geothermometers will give the most reliable results when condensation in the upflow significantly affects the gas concentrations in the steam; reactions with wall rock minerals have relatively less effect on gas ratios. In addition, open system conditions which allow phase separation at pressures above atmospheric will have the same effects as steam condensation (Arnórsson and Gunnlaugsson, 1985).

#### *Gas/ $\text{CO}_2$ geothermometers:*

Geothermometer 1, developed by D'Amore and Panichi (1980), is based on the relative concentrations of  $\text{H}_2\text{S}$ ,  $\text{H}_2$  and  $\text{CH}_4$  to  $\text{CO}_2$  and a fixed  $\text{CO}_2$  partial pressure according to the volume relative ratio in relation to the other gases. Many assumptions of this geothermometer may not be valid for all geothermal systems. Firstly,  $\text{CO}_2$  partial pressure is arbitrarily assigned, and fixed values are defined for the geothermometer (0.1, 1 or 10 bars). Incorrectly selected values will over- or underestimate subsurface temperature by more than  $50^\circ\text{C}$ . This arbitrary selection was criticised by Powell (2000), who found a fairly good correlation between predicted temperature, estimated with  $P_{\text{CO}_2}$  as the geothermometer stated, and that calculated with the actual  $P_{\text{CO}_2}$  of the gas for both reservoir liquid and vapour phases. Besides,  $\text{CH}_4$  is expected to be controlled by free carbon, so this implies that this geothermometer is more appropriate for a sedimentary reservoir, where coal could be present. Then,  $\text{H}_2\text{S}$  is assumed to be controlled by anhydrite and pyrite. These minerals have been found in the Costa Rican and Reykjanes geothermal systems. However, anhydrite is absent at Theistareykir geothermal system, therefore, predicted subsurface temperatures for this area were overestimated by more than  $200^\circ\text{C}$ . Consequently, this geothermometer is not appropriate for either the Costa Rican or the Icelandic geothermal systems considered in this study.

Geothermometer 2, developed by Nehring and D'Amore (1984), is based upon the graphite-carbon dioxide ( $\text{C}/\text{CO}_2$ ) redox pair. This geothermometer is based on the assumption that the aquifer  $\text{H}_2$  concentration is controlled by this redox pair; again, this implies the existence of coal in the reservoir. Besides, the  $\text{C}/\text{CO}_2$  redox buffer reduces more than the ferrous-ferric buffer ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ), so the predicted subsurface temperature is lower than the  $\text{CO}_2$  geothermometer 4 or  $\text{CO}_2/\text{Ar}$  geothermometer 13 (which is based upon the  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ). Similarly, the  $\text{H}_2\text{S}/\text{CO}_2$  geothermometer 3 of these authors is based on the same redox pair and the aquifer  $\text{H}_2\text{S}$  is controlled by pyrite and magnetite. Although pyrite is found in all the geothermal systems studied and magnetite is a primary mineral found in most of the geothermal systems, these geothermometers (2 and 3) are not appropriate for either Costa Rican or Icelandic geothermal systems. In addition, Arnórsson and Gunnlaugsson (1985) criticised that the  $\text{CO}_2/\text{H}_2\text{S}$  ratios do not display any variation with temperature, so cannot be used as a geothermometer.

*Gas/Ar, N<sub>2</sub> geothermometers:*

The H<sub>2</sub>/Ar and CO<sub>2</sub>/Ar geothermometers (12 and 13) were developed by Giggenbach (1991). Similarly, Arnórsson et al. (1998) presented three ratio geothermometers: 20, 21 and 19 (H<sub>2</sub>S/Ar, H<sub>2</sub>/Ar and CO<sub>2</sub>/N<sub>2</sub>). The geothermometers that assumed Ar contents of geothermal fluids are close to those of air-saturated groundwater. This assumption is valid for most geothermal discharges made up predominantly of meteoric waters (Craig, 1963; cited by Giggenbach, 1993). Therefore, Pailas and Borinquen wells, which have been affected by air injection, are not appropriate for evaluation by these ratios geothermometers. The ratio geothermometers of Giggenbach and Arnórsson et al. were calibrated at different temperatures. Therefore, the difference in predicted temperature is due to the solubility of Ar or N<sub>2</sub> at calibration temperatures. The Giggenbach geothermometers assumed air-saturated water at 25°C; the Arnórsson et al. assumed air-saturated water at 5°C (annual mean temperature of Iceland). The solubility of this gas at 25°C is almost half that at 5°C (Nicholson, 1993). Accordingly, the H<sub>2</sub>/Ar geothermometer calibrated at Icelandic conditions will predict lower temperature than that calibrated at 25°C. Predicted subsurface temperature by H<sub>2</sub>/Ar geothermometer 12 for neutral wells at Miravalles and Icelandic geothermal wells is higher than that predicted by geothermometer 21 (Table 4 in Appendix I). Consequently, of these two, geothermometer 12 (H<sub>2</sub>/Ar) is more appropriate for Costa Rican weather conditions. Since argon is a chemically inert gas, ratio geothermometers based on this gas are not affected by physical processes such as secondary boiling or recondensation conditions (Giggenbach, 1991). Therefore, they are useful for fumaroles, where condensation is more prone to occur than in geothermal wells. However, successful application of ratio geothermometers based on Ar depends vitally on the availability of reliable and uncontaminated values for argon.

CO<sub>2</sub>/Ar and H<sub>2</sub>S/Ar geothermometers are based on soluble reactive gases. Among the reactive geothermal gases (H<sub>2</sub>, H<sub>2</sub>S, CH<sub>4</sub> and CO<sub>2</sub>), CO<sub>2</sub> and H<sub>2</sub>S are the slowest in their response to changing conditions such as temperature and redox potential (Giggenbach, 1991). CO<sub>2</sub>/Ar predicts higher subsurface temperature than H<sub>2</sub>S/Ar. Predicted temperature for neutral wells of Miravalles by geothermometer 13 is higher than that by geothermometer 20 when compared with the reference temperature (Table 4 in Appendix I).

CO<sub>2</sub>/N<sub>2</sub> geothermometer 19 theoretically works similarly to CO<sub>2</sub>/Ar 13 since this geothermometer was based on the assumption that N<sub>2</sub> and Ar concentrations in geothermal reservoir waters are equal to those in air-saturated water at 5°C (Arnórsson, 2000). However, these two geothermometers predicted similar subsurface temperatures at low temperature (between 180 and 200°C), but at higher temperature (>250°C) they differed widely (difference in temperature is more than 50°C).

*Gas/H<sub>2</sub> geothermometers:*

As steam approaches the surface it may, on contact with cooler host rocks, condense to a liquid phase which can accumulate to form a perched aquifer. Regardless of whether a secondary aquifer forms, the condensation part of the steam phase will increase the proportion of gas to steam (high gas/steam ratio) remaining in the vapour phase. The steam condensate will dissolve some of the more soluble gases, removing them from the vapour. The twin effects of steam condensation and (partial) removal of the more-soluble gases in the condensate, increases the proportion of the less-soluble gases in the remaining steam (Nicholson, 1993). Steam condensation is caused by cooling during the rise of hot fluids from the deep reservoir to the surface, whereas groundwater addition can remove ammonia due to its relatively high solubility, oxidise hydrogen sulphide to sulphate, and add atmospheric nitrogen and argon (Powell, 2000). Among the gases involved in this study, H<sub>2</sub>S and CO<sub>2</sub> are the most soluble and H<sub>2</sub> the least soluble. Hydrogen solubility is three orders of magnitude smaller than that of H<sub>2</sub>S. Therefore, H<sub>2</sub> removal from the fluid in the upflow is insignificant (Arnórsson and Gunnlaugsson, 1985).

Since condensation processes can affect gases such as CO<sub>2</sub> and H<sub>2</sub>S, geothermometers based on H<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>S ratios have limited success (Giggenbach, 1991). Similarly, CO<sub>2</sub> and H<sub>2</sub>S geothermometers are not recommended due to their high solubility in water. Single gas (H<sub>2</sub>S, H<sub>2</sub> and

CO<sub>2</sub>) geothermometers (5, 7 and 16 of Table 1 in Appendix I) applied to fumarole samples overestimated subsurface temperature compared to its respective gas ratio geothermometers (9 and 11). Comparison between H<sub>2</sub>S and H<sub>2</sub>S/H<sub>2</sub> geothermometers resulted in differences in temperature between 50 and 200°C in Costa Rican fumaroles (RVMF01, RVNT05, RVMT08 and RVMT09). This difference is less (20°C) in the Icelandic fumarole (RV-G1). In the case of H<sub>2</sub> and H<sub>2</sub>/Ar geothermometers, the difference was less than in H<sub>2</sub>S types. CO<sub>2</sub> geothermometer 16, compared with CO<sub>2</sub>/H<sub>2</sub> geothermometer 9, overestimated the subsurface temperature above 400°C with the exception of the basaltic fumarole (RV-G1); there, the difference was 82°C. The difference in temperature between single CO<sub>2</sub> geothermometer and CO<sub>2</sub>/H<sub>2</sub> was larger than that between H<sub>2</sub>S and H<sub>2</sub>S/H<sub>2</sub>.

Two CO<sub>2</sub>/H<sub>2</sub> geothermometers (9 and 10) were developed by Arnórsson and Gunnlaugsson (1985). Geothermometer 9 was calibrated for saline fluids such as in the Costa Rican and Reykjanes geothermal systems, whereas geothermometer 10 was calibrated for dilute fluids (i.e. Theistareykir). Additionally, a gas ratio based on Ar or N<sub>2</sub> can be used for fumaroles, such as CO<sub>2</sub>/Ar, H<sub>2</sub>S/Ar, H<sub>2</sub>/Ar or CO<sub>2</sub>/N<sub>2</sub> (geothermometers 13, 20, 21 and 19, respectively), but the difference in Ar and N<sub>2</sub> solubility regarding the temperature of the area where they are applied should be considered. Geothermometers 11 and 13 predicted subsurface temperatures for Costa Rican RVMT08 (whose gas source is magmatic according to Figure 4) ranging between 261 and 294°C (Table 4 in Appendix I). Geothermometers calibrated for Icelandic conditions (19, 20 and 21) predicted lower subsurface temperatures (between 237 and 252°C). On the other hand, geothermometers 9, 11, 19, 20 and 21 predicted subsurface temperatures for Reykjanes fumarole RV-G1 ranging between 265 and 325°C.

### 6.3.4 Criteria for application of gas geothermometers

During exploration, gas geothermometers are useful tools for estimating subsurface temperature through sampling surface geothermal manifestations such as fumaroles or hot springs. In these cases, vapour and liquid phases do not reach the surface together. Therefore, the gas and water ratio is not available. Gas geothermometers based on gas-gas reactions can be useful in these cases. Nevertheless, as discussed in this study, four geothermometers (1, 2, 3 and 14, Table 1 in Appendix I), based upon gas-gas equilibria, predicted high subsurface temperatures, due to the high temperature (>300°C) needed to attain equilibrium. The results of these geothermometers may indicate deeper temperatures of the reservoir, but care should be taken to avoid misinterpretation. If a low subsurface temperature is predicted by these gas-gas geothermometers, they may indicate a lack of gas-gas equilibrium in deep conditions. Consequently, ratio geothermometers are more appropriate for surface geothermal manifestations. However, single gas geothermometers that are involved in the selected ratio geothermometer should be applied complementarily to ratio geothermometers in order to identify physical processes, such as steam condensation or phase separation, occurring in steam during its rise from the reservoir to the surface.

Gas geothermometers are calibrated for saline and dilute fluids, where redox states are different. Therefore, the selection of a gas geothermometer for a specific area should be based on the salinity or redox state of the geothermal area under evaluation. This criterion should be taken into account for the application of gas geothermometers in wells during evaluation or exploitation. Additionally, meteoric and atmospheric conditions under which the gas geothermometers were calibrated should be considered since gas solubility is a function of temperature.

In addition to the selection of the most representative sampling site, adequate selection in sampling technique and appropriate sampling are essential for the collection of good samples. Air contamination is an external factor that the geochemist should always have in mind prior, during and after sampling. Since air contains reactive gases such as oxygen, absolute concentration of geothermal gases can be different from its original composition. Similarly, adequate selection of an analytical method for gas species is considered important because most geothermal gases, in low concentrations, with the exception of H<sub>2</sub>S and CO<sub>2</sub>, are analysed by volumetric methods. Therefore, it does not mean that a chemical species is not present in the steam, even though it is found to be below the detection

limit of an analytical method. This indicates that the selected analytical method is not adequate for the chemical species. These considerations have to be known by the geochemist responsible for data interpretation in order to avoid misapplication.

Since most of the gas geothermometers are based upon equilibria between geothermal solutions and secondary minerals, the selection of a gas geothermometer for well evaluation or during exploitation should consider fluid chemistry and alteration mineralogy in order to validate and justify the equilibrium assumptions involved in the derivation of geothermometers. The best gas geothermometer for geothermal assessment does not exist. A combination of appropriate single and ratio gas geothermometers is the adequate selection for evaluation of deep and reservoir conditions.

The gas geothermometers evaluated in this study can be arranged in four groups as presented in Table 4. This classification is based on calibration conditions or assumptions involved in the development of the geothermometers. This table is intended to be a quick guide to identify and to select the appropriate gas geothermometers for the geochemist's purposes.

TABLE 4: Classification of 21 gas geothermometers evaluated in this study

Group	Calibration / application	Type	Gases involved	Number*
1	Calibrated for saline (>500 ppm Cl) fluids / oxidising geothermal systems	Single	H <sub>2</sub> S	5
		Single	H <sub>2</sub>	7
		Single	CO <sub>2</sub>	4
		Single	CO <sub>2</sub>	16
		Ratio	H <sub>2</sub> S/H <sub>2</sub>	11
		Ratio	CO <sub>2</sub> /H <sub>2</sub>	9
2	Calibrated for dilute (<500 ppm Cl) fluids / reducing geothermal systems	Single	H <sub>2</sub> S	6
		Single	H <sub>2</sub> S	17
		Single	H <sub>2</sub>	8
		Single	H <sub>2</sub>	18
		Single	CO <sub>2</sub>	15
		Ratio	CO <sub>2</sub> /H <sub>2</sub>	10
3	Based on Ar or N <sub>2</sub> in air saturated water	At 25°C	H <sub>2</sub> /Ar	12
		At 25°C	CO <sub>2</sub> /Ar	13
		At 5°C	H <sub>2</sub> /Ar	21
		At 5°C	H <sub>2</sub> S/Ar	20
		At 5°C	CO <sub>2</sub> /N <sub>2</sub>	19
4	Based on gas-gas equilibria	Ratio	Gas/CO <sub>2</sub>	1
		Ratio	H <sub>2</sub> /CO <sub>2</sub>	2
		Ratio	H <sub>2</sub> S/CO <sub>2</sub>	3
		Ratio	CH <sub>4</sub> /CO <sub>2</sub>	14

\*Number of geothermometer referred to in Table 1 in Appendix I

## 7. CONCLUSIONS

Regarding the high-temperature (230-310°C) andesitic geothermal systems (Miravalles, Pailas and Borinquen, with a concentration of chloride from 3,000 to 5,000 ppm) of Costa Rica and basaltic geothermal systems of Reykjanes (saline fluids with 18,000-20,000 ppm of chloride) and Theistareykir (dilute fluid with <500 ppm of chloride) of Iceland, this study concludes the following:

- Aquifer partial pressure of H<sub>2</sub>S in saline andesitic and basaltic geothermal fluids is controlled by equilibrium with three mineral assemblage buffers: anhydrite-clinozoisite-magnetite-prehnite-



pyrite-quartz, hematite-magnetite-pyrite, and anhydrite-magnetite-pyrite-quartz-wollastonite; whereas, in dilute fluids, H<sub>2</sub>S partial pressure is controlled by the magnetite-pyrrhotite-pyrite assemblage buffer.

- Aquifer partial pressure of H<sub>2</sub> in saline geothermal systems is potentially controlled by the same assemblage buffers that constrain H<sub>2</sub>S, whereas partial pressure of H<sub>2</sub> in the dilute high-temperature geothermal system of Theistareykir is clearly controlled by the epidote-pyrrhotite-pyrite-prehnite assemblage buffer.
- Aquifer partial pressure of CO<sub>2</sub> in saline andesitic and basaltic geothermal systems is controlled by the calcite-clinozoisite-prehnite-quartz assemblage buffer.
- Aquifer partial pressure of H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> in high-temperature andesitic acid (aquifer pH < 5) and bicarbonate (aquifer aqueous CO<sub>2</sub> above 20,000 ppm) geothermal fluids may be due to either lack of equilibrium of these fluids with alteration mineralogy or perhaps the fluids are potentially controlled by reduced buffers such as epidote-pyrrhotite-pyrite-prehnite and magnetite-pyrrhotite-pyrite.
- Single H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> geothermometers (5, 7 and 16, respectively) calibrated for saline fluids are appropriate for the neutral wells of Miravalles and the Reykjanes wells; whereas single H<sub>2</sub>S (6 and 17) and H<sub>2</sub> (8 and 18) geothermometers calibrated for dilute fluids are appropriate for Theistareykir wells.
- Geothermal wells affected by air injection during evaluation should use gas geothermometers involving only geothermal gases such as H<sub>2</sub>S, H<sub>2</sub> or CO<sub>2</sub>, whose aquifer partial pressure's approach to equilibrium pressure is controlled by its respective mineral assemblage buffer.
- Gas ratio geothermometers based on argon or nitrogen are applied at atmospheric conditions at which the geothermometers were calibrated: geothermometers from Arnórsson et al. (1998) CO<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>S/Ar and H<sub>2</sub>/Ar are appropriate for areas whose annual mean temperature is 5°C (i.e. Iceland); geothermometers from Giggenbach (1991), H<sub>2</sub>/Ar and CO<sub>2</sub>/Ar, are effective for areas of annual mean temperature of 25°C. Geothermometers from Arnórsson and Gunnlaugsson (1985) CO<sub>2</sub>/H<sub>2</sub> and H<sub>2</sub>S/H<sub>2</sub> are appropriate for saline geothermal manifestations, while the geothermometer CO<sub>2</sub>/H<sub>2</sub> is effective for dilute fluids.

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## NOMENCLATURE

Name	Symbol	Equation
Anhydrite	anh	$CaSO_4$
Calcite	cal	$CaCO_3$
Clinozoisite	czo	$Ca_2Al_3Si_3O_{12}(OH)$
Epidote	epi	$Ca_2FeAl_2Si_3O_{12}(OH)$
Hematite	hem	$Fe_2O_3$
Magnetite	mag	$Fe_3O_4$
Prehnite	pre	$Ca_2Al_2Si_3O_{10}(OH)_2$
Pyrrhotite	po	$FeS$
Pyrite	py	$FeS_2$
Quartz	qtz	$SiO_2$
Wollastonite	wol	$CaSiO_3$

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## APPENDIX I: Tables with chemical equations and chemical data

TABLE 1: Equations for gas geothermometers

Source	Equation	Condition
D'Amore and Panichi, 1980 (mol % dry gas)	$T(^{\circ}\text{C}) = \frac{24775}{2 \log \frac{CH_4}{CO_2} - 6 \log \frac{H_2}{CO_2} - 3 \log \frac{H_2S}{CO_2} - 7 \log P_{CO_2} + 36.05} - 273.15$	1 $[CO_2] < 75 \text{ mol}\%$ , $P_{CO_2} = 0.1 \text{ atm}$ ; $[CO_2] > 75 \text{ mol}\%$ , $P_{CO_2} = 1 \text{ atm}$ ; $[CO_2] > 75 \text{ mol}\%$ and $[CH_4] > 2[H_2]$ and $[H_2S] > 2[H_2]$ , $P_{CO_2} = 10 \text{ atm}$ .
Nehring and D'Amore, 1984 (mmol/kg)	$T(^{\circ}\text{C}) = 190.3 + 55.97 \left( \log H_2 + \frac{1}{2} \log CO_2 \right) - 0.14 \left( \log H_2 + \frac{1}{2} \log CO_2 \right)^2$ $T(^{\circ}\text{C}) = 194.3 + 56.44 \left( \log H_2S + \frac{1}{6} \log CO_2 \right) + 1.53 \left( \log H_2S + \frac{1}{6} \log CO_2 \right)^2$ $T(^{\circ}\text{C}) = -44.1 + 269.25 \log CO_2 - 76.88 (\log CO_2)^2 + 9.52 (\log CO_2)^3$	2 3 4 For all waters
Arnórsson and Gunnlaugsson, 1985 (mmol/kg)	$T(^{\circ}\text{C}) = 246.7 + 44.81 \log H_2S$ $T(^{\circ}\text{C}) = 173.2 + 65.04 \log H_2S$ $T(^{\circ}\text{C}) = 277.2 + 20.99 \log H_2$ $T(^{\circ}\text{C}) = 212.2 + 38.59 \log H_2$ $T(^{\circ}\text{C}) = 341.7 - 28.57 \log \frac{CO_2}{H_2}$ $T(^{\circ}\text{C}) = 311.7 - 66.72 \log \frac{CO_2}{H_2}$ $T(^{\circ}\text{C}) = 304.1 - 39.48 \log \frac{H_2S}{H_2}$	5 6 7 8 9 10 11 For all waters in the range between 200°C and 300°C and Cl <sup>-</sup> > 500 ppm For all waters below 200°C and Cl <sup>-</sup> < 500 ppm For all waters in the range between 200°C and 300°C and Cl <sup>-</sup> > 500 ppm For all waters below 200°C and Cl <sup>-</sup> < 500 ppm For all waters in the range between 200°C and 300°C and Cl <sup>-</sup> > 500 ppm For all waters below 200°C and Cl <sup>-</sup> < 500 ppm For all waters in the range between 200°C and 300°C and Cl <sup>-</sup> > 500 ppm

TABLE 1 cont.: Equations for gas geothermometers

Source	Equation	Condition
	$T(^{\circ}\text{C}) = 70 \left( 2.5 + \log \frac{H_2}{Ar} \right)$	12 Calibrated with Ar concentrations corresponding with that of air saturated water at 25°C
Giggenbach, 1991 (mol% dry gas)	$T(^{\circ}\text{C}) = 49.794 + 78.076 \left( \log \frac{CO_2}{Ar} \right) - 7.7062 \left( \log \frac{CO_2}{Ar} \right)^2 + 0.8546 \left( \log \frac{CO_2}{Ar} \right)^3 - 0.0395 \left( \log \frac{CO_2}{Ar} \right)^4$	13 Calibrated with Ar concentrations corresponding with that of air saturated water at 25°C Derived from equation: $\log \frac{CO_2}{Ar} = -7.53 + 0.0277T + \frac{2048}{T + 273.15}$
	$T(^{\circ}\text{C}) = \frac{4625}{10.4 + \log \frac{CH_4}{CO_2}} - 273.15$	14
	$T(^{\circ}\text{C}) = 121.8 + 72.012(\log CO_2) - 11.068(\log CO_2)^2 + 4.724(\log CO_2)^3$	15 Valid for $a_{epi}=0.3$ ; mineral composition of -0.155
	$T(^{\circ}\text{C}) = 129.2 + 88.299(\log CO_2) - 21.946(\log CO_2)^2 + 10.103(\log CO_2)^3$	16 Valid for $a_{epi}=0.7$ ; mineral composition of -0.523
	$T(^{\circ}\text{C}) = 177.6 + 66.152(\log H_2 S) + 4.811(\log H_2 S)^2$	17 Mineral composition of +0.104
	$T(^{\circ}\text{C}) = 227.1 + 56.168(\log H_2) + 5.836(\log H_2)^2 + 6.63(\log H_2)^3$	18 Mineral composition of +0.104
Arnórsson et al., 1998 (mmol/kg)	$T(^{\circ}\text{C}) = 173.2 + 48.751 \left( \log \frac{CO_2}{N_2} \right) + 7.599 \left( \log \frac{CO_2}{N_2} \right)^2 + 1.739 \left( \log \frac{CO_2}{N_2} \right)^3$	19 Calibrated with N <sub>2</sub> concentrations corresponding with that of air saturated water at 5°C
	$T(^{\circ}\text{C}) = 137.6 + 42.265 \left( \log \frac{H_2 S}{Ar} \right) + 4.108 \left( \log \frac{H_2 S}{Ar} \right)^2$	20 Calibrated with Ar concentrations corresponding with that of air saturated water at 5°C
	$T(^{\circ}\text{C}) = 170 + 43.26 \left( \log \frac{H_2}{Ar} \right) + 0.64 \left( \log \frac{H_2}{Ar} \right)^2$	21 Calibrated with Ar concentrations corresponding with that of air saturated water at 5°C



TABLE 2: Chemical reactions and equations of mineral assemblages potentially controlling concentrations of H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub>

Gas	Mineral buffer	Reaction	Equation
H <sub>2</sub> S	epi-po-py-pre	$FeS_2 + FeS + 2Ca_2Al_2Si_3O_{10}(OH)_2 + 2H_2O_1 \rightleftharpoons 2Ca_2FeAl_2Si_3O_{12}(OH) + 3H_2S_{aq}$	$\log a_{H_2S} = \frac{1}{3}(\log K - 2 \log a_{epi} + 2 \log a_{pre,Al})$
	anh-czo-mag-pre-py-qtz	$\frac{3}{2}Ca_2Al_2Si_3O_{10}(OH)_2 + 6FeS_2 + 10H_2O_1 \rightleftharpoons Ca_2Al_3Si_3O_{12}(OH) + CaSO_4 + \frac{3}{2}SiO_2 + 2Fe_3O_4 + 11H_2S_{aq}$	$\log a_{H_2S} = \frac{1}{22}(\log K - 2 \log a_{czo} + 3 \log a_{pre,Al})$
	mag-po-py	$FeS_2 + 2FeS + 4H_2O_1 \rightleftharpoons Fe_3O_4 + 4H_2S_{aq}$	$\log a_{H_2S} = \frac{1}{4} \log K$
	hem-mag-py	$FeS_2 + Fe_3O_4 + 2H_2O_1 \rightleftharpoons 2Fe_2O_3 + 2H_2S_{aq}$	$\log a_{H_2S} = \frac{1}{2} \log K$
	anh-mag-py-qtz-wol	$CaSiO_3 + 6FeS_2 + 11H_2O_1 \rightleftharpoons CaSO_4 + SiO_2 + 2Fe_3O_4 + 11H_2S_{aq}$	$\log a_{H_2S} = \frac{1}{11} \log K$
H <sub>2</sub>	epi-po-py-pre	$4FeS + 2Ca_2Al_2Si_3O_{10}(OH)_2 + 2H_2O_1 \rightleftharpoons 2Ca_2FeAl_2Si_3O_{12}(OH) + 2FeS_2 + 3H_2_{aq}$	$\log a_{H_2} = \frac{1}{3}(\log K - 2 \log a_{epi} + 2 \log a_{pre,Al})$
	anh-czo-mag-pre-py-qtz	$9Ca_2Al_2Si_3O_{10}(OH)_2 + 3FeS_2 + 16H_2O_1 \rightleftharpoons 6Ca_2Al_3Si_3O_{12}(OH) + 6CaSO_4 + 9SiO_2 + Fe_3O_4 + 22H_2_{aq}$	$\log a_{H_2} = \frac{1}{22}(\log K - 6 \log a_{czo} + 9 \log a_{pre,Al})$
	mag-po-py	$6FeS + 4H_2O_1 \rightleftharpoons 3FeS_2 + Fe_3O_4 + 4H_2_{aq}$	$\log a_{H_2} = \frac{1}{4} \log K$
	hem-mag	$2Fe_3O_4 + H_2O_1 \rightleftharpoons 3Fe_2O_3 + H_2_{aq}$	$\log a_{H_2} = \log K$
	anh-mag-py-qtz-wol	$3FeS_2 + 6CaSiO_3 + 22H_2O_1 \rightleftharpoons Fe_3O_4 + 6CaSO_4 + 6SiO_2 + 22H_2_{aq}$	$\log a_{H_2} = \frac{1}{22} \log K$
CO <sub>2</sub>	cal-czo-pre-qtz	$2Ca_2Al_3Si_3O_{12}(OH) + 2CaCO_3 + 3SiO_2 + 2H_2O_1 \rightleftharpoons 3Ca_2Al_2Si_3O_{10}(OH)_2 + 2CCO_{2,aq}$	$\log a_{CO_2} = \frac{1}{2}(\log K - 3 \log a_{pre,Al} + 2 \log a_{czo})$
FT	Gas-gas reaction	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O_1$	$\log a_{CO_2} - \log a_{CH_4} - 4 \log a_{H_2} = \log K$

TABLE 3: Corrected gas concentrations at atmospheric conditions (1 bar-a and 100°C) and molar ratio of the Costa Rican and Icelandic geothermal fluids

Well	Date	mmol/kg steam						Molar ratio	
		CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	Ar	N <sub>2</sub> /Ar	CO <sub>2</sub> /N <sub>2</sub>
PGM-02	05/02/2010	218	2.23	0.183	0.248	0.877	0.035	25	248
PGM-02	28/11/2009	213	2.43	0.149	0.238	0.959	0.010	97	222
PGM-02	21/08/2009	215	2.40	0.146	0.223	0.848	0.010	97	222
PGM-07	05/02/2010	373	5.54	0.464	0.709	1.274	0.012	106	293
PGM-07	28/11/2009	349	5.47	0.366	0.624	0.986	0.008	118	354
PGM-07	21/08/2009	357	5.40	0.391	0.633	1.118	0.010	110	320
PGM-14	06/02/2008	59.17	0.64	0.072	0.049	0.826	0.012	67	72
PGM-14	11/10/2007	68.00	0.98	0.014	0.033	0.641	0.006	115	106
PGM-14	20/06/2007	68.72	1.02	0.022	0.043	1.067	0.015	71	64
PGM-17	29/11/2009	60.03	0.70	0.032	0.021	0.592	0.008	79	101
PGM-17	21/10/2008	63.75	1.02	0.044	0.029	0.581	0.007	78	110
PGM-17	06/02/2008	63.99	0.56	0.054	0.040	0.455	0.007	70	141
PGM-21	08/07/2009	47.97	0.72	0.037	0.026	0.424	0.005	80	113
PGM-21	24/06/2008	70.83	0.89	0.036	0.021	0.346	0.005	67	205
PGM-21	14/02/2008	67.24	0.60	0.034	0.027	0.298	0.004	77	225
PGM-29	17/11/2009	2,338	3.82	0.599	0.764	9.306	0.052	178	251
PGM-29	10/07/2009	2,307	1.59	0.549	0.904	9.391	0.065	145	246
PGM-29	14/02/2008	2,894	3.31	0.557	1.105	11.65	0.081	144	249
PGM-43	26/06/2008	12.16	0.70	0.041	0.009	1.213	0.016	76	10
PGM-43	22/11/2007	12.61	0.51	0.029	0.016	0.502	0.007	70	25
PGM-43	13/02/2007	14.06	0.59	0.017	0.008	0.698	0.008	88	20
PGM-44	23/06/2009	36.45	0.81	0.080	0.031	2.123	0.029	73	17
PGM-44	25/02/2009	34.93	0.99	0.032	0.028	2.164	0.030	73	16
PGM-44	14/11/2008	33.29	0.83	0.032	0.023	2.486	0.031	80	13
PGM-49	17/03/2009	196	0.55	0.006	0.110	3.404	0.045	75	58
PGM-49	03/07/2007	144	0.40	0.020	0.043	1.814	0.027	68	79
PGM-49	14/02/2007	129	0.69	0.041	0.051	2.374	0.033	73	54
PGP-01	02/03/2010	15.55	0.84	0.039	0.078	6.972	0.096	73	2
PGP-03	13/11/2008	13.17	1.00	0.162	0.039	10.34	0.117	88	1
PGP-04	13/09/2008	9.87	1.25	0.515	0.047	4.453	0.043	103	2
PGP-08	16/05/2009	42.29	1.13	0.091	0.098	5.805	0.073	80	7
PGP-12	18/12/2009	14.45	1.26	0.000	0.052	4.865	0.069	71	3
PGP-24	05/02/2010	6.79	0.74	0.000	0.022	3.541	0.051	69	2
PGB-01	24/07/2010	29.73	0.66	0.000	0.033	9.760	0.111	88	3
RVMF01	10/02/2006	22,248	201	0.000	3.941	228	1.852	123	98
RVNT05	10/02/2006	22,101	224	0.000	1.287	78.16	1.877	42	283
RVMT08	24/07/2000	8,577	166	92.94	6.916	714	1.333	536	12
RVMT09	24/07/2000	23,099	202	0.058	35.49	1,256	13.61	92	18
RVMT09	24/07/2000	23,478	216	0.053	33.13	1,264	13.21	96	19
RVMT09	24/07/2000	25,445	241	0.047	35.70	1,677	16.27	103	15
RN-10	09/06/2006	104	6.06	0.184	0.016	0.639	0.017	41	146
RN-12	14/06/2006	96.33	3.74	0.184	0.011	1.077	0.021	56	80
RN-19	14/06/2006	57.16	2.34	0.149	0.004	0.941	0.017	59	54
RV-G1	01/09/2006	155	11.15	2.011	0.024	1.243	0.015	48	125
TG-01	10/03/2008	10.90	5.48	3.631	0.003	0.545	0.012	48	18
TG-03	26/03/2007	18.49	11.14	7.977	0.004	1.244	0.025	54	13
TG-06	02/12/2008	54.68	10.30	4.604	0.002	0.700	0.012	66	69

TABLE 4: Median of calculated subsurface temperature (°C) by the application of 21 gas geothermometers to Costa Rican and Icelandic geothermal fluids

Well	Gas/CO <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>	H <sub>2</sub> S/CO <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /H <sub>2</sub>	CH <sub>4</sub> /CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> S/Ar	H <sub>2</sub> /Ar	T <sub>R</sub>				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	238
PGM-02	244	209	239	286	264	198	260	180	252	101	256	257	299	348	289	344	203	181	357	261	221	238
PGM-07	257	239	262	301	280	221	269	196	257	114	259	286	309	331	312	380	229	205	370	283	240	241
PGM-14	231	149	211	250	246	173	242	148	242	78	238	204	268	369	246	279	177	119	301	229	188	237
PGM-17	251	165	202	247	240	163	249	160	251	101	251	229	280	382	243	276	167	145	319	237	204	235
PGM-21	249	159	202	249	240	164	247	156	248	92	253	234	290	388	245	279	168	138	348	250	207	233
PGM-29	191	272	258	354	270	207	272	202	238	70	274	240	309	389	419	564	213	213	357	216	211	232
PGM-43	300	135	192	172	236	158	245	153	266	136	255	204	247	363	194	213	162	131	254	230	188	232
PGM-44	270	150	204	223	243	168	246	155	255	110	248	178	238	361	224	250	172	134	246	207	172	230
PGM-49	196	156	201	275	235	156	242	147	232	55	253	167	266	388	273	319	161	117	292	193	165	220
PGP-01	292	145	201	184	243	168	248	158	168	138	252	148	170	298	200	220	173	141	191	181	153	243
PGP-03	365	177	205	174	247	173	261	182	187	184	273	185	159	314	195	215	177	183	178	180	176	246
PGP-04	439	202	209	157	251	179	271	201	205	226	289	250	179	300	187	205	184	211	191	208	217	225
PGP-08	284	178	213	231	249	177	255	172	166	134	261	182	204	322	230	258	181	168	222	194	174	235
PGP-12	NA	NA	211	180	251	180	NA	NA	NA	NA	NA	NA	177	308	198	218	184	NA	198	198	NA	244
PGP-24	NA	NA	195	132	241	165	NA	NA	NA	NA	NA	NA	164	312	177	193	169	NA	188	192	NA	247
PGB-01	NA	NA	198	216	239	162	NA	NA	NA	NA	NA	NA	184	348	219	244	166	NA	199	173	NA	241
RVMF01	NA	NA	379	456	350	323	NA	NA	NA	NA	NA	NA	275	423	614	928	356	NA	314	241	NA	NA
RVNT05	NA	NA	382	455	352	326	NA	NA	NA	NA	NA	NA	274	477	613	927	360	NA	364	243	NA	NA
RVMT08	349	408	369	405	346	318	319	288	186	181	294	304	261	360	521	752	348	411	237	244	252	NA
RVMT09	117	feitt	382	460	352	325	250	163	180	NA	161	NA	246	339	622	944	359	151	249	193	NA	NA
RN-10	324	205	259	264	282	224	262	184	263	128	244	249	273	426	261	301	232	186	337	272	215	310
RN-12	321	205	247	262	272	210	262	184	264	130	252	244	267	436	258	297	217	186	310	254	211	295
RN-19	341	193	232	243	263	197	260	180	268	139	257	243	259	457	240	271	203	181	294	246	211	275
RV-G1	412	268	277	277	294	241	284	224	288	186	275	307	273	429	276	323	252	245	325	292	265	NA
TG-01	NA	251	247	163	280	221	289	234	328	280	297	350	232	NA	190	208	229	262	253	278	281	290
TG-03	737	276	268	193	294	241	296	247	331	287	298	353	227	413	205	226	252	287	244	278	282	290
TG-06	584	276	270	242	292	239	291	238	311	240	290	360	267	509	238	269	250	269	305	298	287	300

FT: Fischer-Tropsch. Tr: Reference temperature. NA: no data

TABLE 5: Computed chloride concentration and partial pressure of CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>, and CH<sub>4</sub> in the Costa Rican and Icelandic deep fluid compositions

Well	Date	Cl (ppm)	Partial pressure (bar-a)			
			CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	CH <sub>4</sub>
PGM-02	05/02/2010	2,965	4.730	0.0203	0.0209	0.0274
PGM-07	05/02/2010	3,267	8.220	0.0498	0.0527	0.0778
PGM-14	06/02/2008	3,169	1.260	0.0075	0.0082	0.0055
PGM-17	29/11/2009	3,581	1.260	0.0053	0.0037	0.0024
PGM-21	08/07/2009	3,935	0.988	0.0527	0.0043	0.0029
PGM-29	17/11/2009	3,387	49.10	0.0323	0.0684	0.0842
PGM-43	26/06/2008	3,667	0.245	0.0061	0.0047	0.0010
PGM-44	25/02/2009	3,577	0.698	0.0077	0.0037	0.0031
PGM-49	14/02/2007	3,628	2.480	0.0067	0.0048	0.0056
PGP-01	02/03/2010	4,876	0.311	0.0060	0.0045	0.0086
PGP-03	13/11/2008	5,074	0.282	0.0103	0.0182	0.0042
PGP-04	13/09/2008	4,857	0.181	0.0078	0.0595	0.0052
PGP-08	16/05/2009	4,756	0.884	0.0089	0.0105	0.0109
PGP-12	18/12/2009	4,636	0.304	0.0098	0.0000	0.0057
PGP-24	18/12/2009	4,935	0.144	0.0062	0.0000	0.0023
PGB-01	24/07/2010	4,863	0.630	0.0068	0.0000	0.0036
RN-10	09/06/2006	18,168	2.440	0.0641	0.0149	0.0012
RN-12	14/06/2006	18,665	2.370	0.0408	0.0171	0.0010
RN-19	14/06/2006	19,526	1.450	0.0256	0.0163	0.0005
TG-01	10/03/2008	98	0.263	0.0516	0.3530	0.0003
TG-03	26/03/2007	79	0.446	0.1040	0.7760	0.0003
TG-06	02/12/2008	41	1.210	0.0798	0.4120	0.0001

TABLE 6: Logarithm of equilibrium constant (Log K) of mineral assemblage equilibria for H<sub>2</sub>S, H<sub>2</sub> and CO<sub>2</sub> and Fischer-Tropsch (FT) reaction at different temperatures

Gas	MB	Temperature (°C) / Log K								
		150	175	200	225	250	275	300	325	350
H <sub>2</sub> S	1	-8.916	-7.244	-5.765	-4.448	-3.268	-2.206	-1.245	-0.372	0.425
	2	-93.99	-80.38	-68.32	-57.58	-47.95	-39.26	-31.40	-24.26	-17.72
	3	-12.50	-10.54	-8.809	-7.280	-5.917	-4.697	-3.599	-2.606	-1.706
	4	-7.710	-6.646	-5.705	-4.869	-4.122	-3.452	-2.847	-2.299	-1.801
	5	-44.04	-37.60	-31.90	-26.84	-22.30	-18.21	-14.52	-11.17	-8.106
H <sub>2</sub>	6	-3.173	-2.603	-2.113	-1.691	-1.325	-1.006	-0.728	-0.484	-0.273
	7	-102.4	-91.21	-81.29	-72.44	-64.49	-57.33	-50.83	-44.92	-39.53
	8	-4.842	-4.347	-3.940	-3.604	-3.327	-3.098	-2.910	-2.756	-2.637
	9	-3.402	-3.153	-2.936	-2.745	-2.577	-2.429	-2.298	-2.183	-2.081
	10	-84.63	-75.66	-67.75	-60.72	-54.44	-48.82	-43.743	-39.15	-34.99
CO <sub>2</sub>	11	-0.528	0.024	0.508	0.934	1.311	1.647	1.948	2.218	2.461
FT	12	9.901	8.191	6.666	5.299	4.067	2.951	1.937	1.010	0.160

MB: mineral buffer referred to Table 2 in Appendix I