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GEOTHERMAL TRAINING PROGRAMME



LaGeo S.A. de C.V.

GEOTHERMOMETRY

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ABSTRACT

The geothermometers have been one of the major achievements of fluid geochemistry; they are very useful especially in the exploration and development phases. In Costa Rica two of the three groups of geothermometers, the water and gas geothermometers, have been applied in the exploration and development phases during the investigations at the Miravalles, Rincón de la Vieja (Pailas, Borinquen and North Sector) Tenorio, Poco Sol and Platanar-Porvenir geothermal areas and also during the development and exploitation phases of the Miravalles and Pailas geothermal fields. The water geothermometers applied at the different areas were the Na/K, Na-K-Ca, K-Mg, silica and Na-K-Mg diagrams while the gas geothermometers were D'Amore and Panichi, H₂-Ar, CO₂-Ar both from Giggenbach and others. A brief discussion of these results are presented in this paper

1. INTRODUCTION

Where fluids reach the surface by way of hot springs, fumaroles or wells, their chemical composition may often be used to deduce sub-surface temperatures. Concentrations of the constituents that relate to deep temperatures are called chemical geothermometers and are very useful as a prospecting tool especially in the exploration and development stages. The geothermometers probably are one of the most important tools in these phases but they are also very useful during the exploitation mainly in the monitoring of the response of the geothermal reservoir to the production load.

The interpretation of the geothermometer data should be done carefully and it should always be kept in mind that the geothermal fluids are coming from the deep reservoir where the most important process is water-rock interaction, which is dependent mainly on temperature, and has a great influence on the chemical composition of the fluids. Both characteristics make the geothermometers work. On the other hand, when the geothermal fluids rise to the surface they may cool by conductive heat loss as they travel through cooler rocks or by boiling because of decreasing hydrostatic head. All of these processes produce changes in the composition of the rising fluids. The conductive cooling can cause some modifications in the chemical composition of the ascending water by mineral dissolution or precipitation because the cooling may change its degree of saturation with respect to both primary and secondary minerals and may affect the estimated temperature. However, the boiling processes invariably cause changes in the

composition of rising geothermal fluid, because the temperature decrease and saturation degree varies and mineral dissolution or precipitation can occur affecting the estimated temperature. Another very important process that occurs in the top of the geothermal system is the mixing with ground waters which causes dilution and cools the geothermal fluids.

As mentioned before the geothermometers depend primarily on one or more dissolved constituents in the geothermal fluid whose concentrations vary depending on the temperature of the fluids. These constituents may be solutes, gases or isotopes. Geothermometers have been classified into three groups:

- Solute geothermometers;
- Gas geothermometers;
- Isotope geothermometers

The first two geothermometers are called chemical geothermometers.

Geothermometers used in geothermal exploration have been developed by many individuals. Here, the section by D'Amore and Arnorsson (2000) from the book by Arnorsson (2000) is used as a general reference for this information. Even though many of these references are cited here, for further information on them, the reader is referred to that source.

2. CHEMICAL GEOTHERMOMETERS

Chemical geothermometers depend on the existence at depth of a temperature dependant mineral-fluid equilibrium which must be preserved during the passage of fluid to the surface. This statement must always be kept in mind, and it comprises the following assumptions:

1. Fluid-mineral equilibrium at depth.
2. A temperature dependant reaction at depth.
3. An adequate supply of solid phases to permit the fluid to become saturated with respect to the constituents used for Geothermometry.
4. Negligible re-equilibrium as the water flows to the surface.
5. No dilution or mixing of hot and cold waters.

The first three assumptions are probably good for a few reactions that occur in many places. The last two are probably not valid for many geothermal fluids since the information obtained is only from the upper part of those systems.

Near neutral pH alkali chloride waters are the most informative for geothermometry. However, acid sulphate waters in which constituents are leached from surface rocks are not suitable as geothermometers. In addition, fluids from geothermal systems in which sea water circulates give misleading temperatures because the high salinities prevent the establishment of a fluid-mineral equilibrium. Many different geothermometers have been suggested; however, we only have to consider a few solute ones briefly.

2.1 Solute geothermometers

Many solute (water) geothermometers have been developed; the most used are the silica (quartz and chalcedony), Na/K, Na-K-Ca and many others like Na/Li, Li/Mg, K/Mg ratios and Na-K-Mg relationships.

2.1.1 Silica geothermometers

Bodvarsson (1960) suggested an empirical and qualitative silica geothermometer based on studies in Iceland. Experimental studies on quartz solubility were carried out by Kennedy (1950) and Morey et al. (1962) establishing the theory behind silica geothermometer usage. Mahon (1966) showed that silica in New Zealand geothermal waters was controlled by quartz solubility, and Fournier and Rowe (1966) formulated a method for determining reservoir temperatures.

Considerations:

- Works best for waters having subsurface $T > 150^{\circ}\text{C}$.
- Effects of steam separation are due to subsurface boiling.
- Polymerization or precipitation of SiO_2 before sampling.
- Dissolved SiO_2 controlled by solids other than quartz.
- Effect of pH on quartz solubility.
- Dilution.

Temperature range - experimentally derived equations describing quartz solubility are good between 0-250°C accurate to about $\pm 2^{\circ}\text{C}$; at $>250^{\circ}\text{C}$ different equations are required to describe quartz solubility. Steam separation (adiabatic vs. conductive cooling)—vigorously boiling hot springs with mass flows greater than 120-130 kg/minute ($\approx \text{kg/sec}$) are assumed to have cooled adiabatically (rapid fluid ascent, no heat loss to surrounding rocks during boiling) and therefore an equation which corrects for the concentration of silica in the liquid due to steam loss is used (silica does not vaporize upon boiling). For springs discharging at reduced flow rates and temperatures lower than boiling, a combination of adiabatic and conductive cooling is likely. Trusdell et al. (1977) discussed this point further and showed that for a reservoir fluid at 200°C and 500 m depth that conductive cooling occurs between 200 and 100°C if the fluid rises at less than 13 kg/min (spring discharge $< 0.2 \text{ kg/sec}$).

Precipitation of silica before sampling - quartz rapidly dissolves in water (in a few hours to days) at temperatures between 200-250°C within a pH range of 5-8 and is favoured at higher salinities. At $T > 225^{\circ}\text{C}$ a rising fluid will become supersaturated with respect to amorphous silica before cooling to 100°C; therefore surface samples will give maximum subsurface temperatures of 225°C due to subsurface precipitation of amorphous silica.

Precipitation of silica after sampling - an untreated water sample will cool during storage causing dissolved silica to polymerize with or without precipitation of amorphous silica within the sample bottle. In order to keep all the silica in the solution in monomer form, some part of the aqueous sample needs to be diluted (5-10 ml sample pipette into 50 ml of silica-free water). Two analytical techniques are employed for silica determination: atomic absorption spectrometry (AAS) and the colorimetric technique; AAS can detect both monomeric and polymeric silica forms whereas the colorimetric technique detects monomeric silica only, unless treated.

Silica solubility: quartz is the most stable and least soluble form of solid silica, and in general it controls silica solubility in geothermal waters $> 150^{\circ}\text{C}$. However other solid silica compounds exist (chalcedony, amorphous silica) having higher solubilities than quartz and where they are in contact with the solution they control silica solubility preferentially over quartz below this temperature (Fournier, 1973).

pH effect: quartz solubility increases with increasing pH (alkaline solutions); however, this is not much of a problem for many geothermal fluids, despite tending to be alkaline in surface discharges. This is because for most cases alkalinity in chloride waters is due to boiling and CO_2 loss. Under this condition,

dissolved silica is gained in the reservoir, where pH tends to be neutral to slightly acidic, before much boiling has occurred. In some very rare circumstances a correction for pH may be required.

Dilution: Subsurface dilution of the geothermal fluid decreases the silica content. If equilibrium between fluid and rock is achieved, the silica geothermometer will give a temperature reflecting these cooler conditions; alternatively, if equilibrium is not attained then the silica geothermometer will give erroneous temperatures that are too cool.

The silica geothermometers used mostly by our geochemistry group are the following:

Quartz- no steam loss (25-250°C), Fournier (1977), it is applied mainly to downhole samples:

$$t^{\circ}\text{C} = \frac{1309}{5.19 - \log(\text{SiO}_2)} - 273.15$$

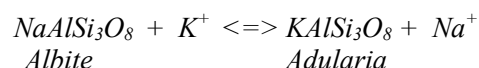
Quartz maximum steam loss (25-250°C), Fournier (1977), which is applied mainly to springs and water wells separated to atmospheric pressure.

$$t^{\circ}\text{C} = \frac{1522}{5.75 - \log(\text{SiO}_2)} - 273.15$$

2.1.2 Na/K geothermometers

Historic information: Several investigators noted the systematic variations in Na/K contents with temperature based on natural fluids and experimental studies (White, 1965; Ellis and Mahon, 1967; Fournier and Truesdell, 1973; Fournier, 1979; Giggenbach et al., 1983).

Considerations: The basis for this geothermometer assumes that fluids have equilibrated with sodium-bearing feldspar (albite) and potassium-bearing feldspar (adularia) which are common and abundant hydrothermal minerals:



This geothermometer works best for fluids derived from a thermal environment > 180°C, containing low calcium ($c_{\text{Ca}}^{1/2}/c_{\text{Na}} < 1$). The main advantage of this geothermometer is that it is less affected by dilution and steam separation than other geothermometers, assuming that the diluting fluid contains little sodium or potassium. Also, the flow rate of a spring may be less than that required for the application of the quartz geothermometer.

The Na-K geothermometers that have been used by our geochemistry group are the following:

Na-K geothermometer, (100-275°C), Truesdell 1976, it is used in the exploration phase on spring samples:

$$t^{\circ}\text{C} = \frac{856}{\log(\text{Na/K}) + 0.857} - 273.15$$

Na-K geothermometer, Giggenbach 1988, ($t > 180^\circ\text{C}$), it is used in the exploration and development phases, applied on spring and deep well samples:

$$t^\circ\text{C} = \frac{1390}{1.750 + \log(\text{Na}/\text{K})} - 273.15$$

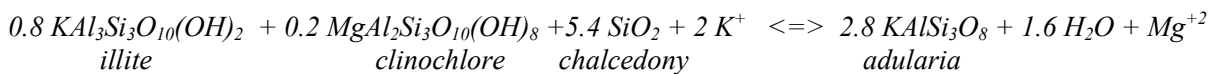
Na-K geothermometer, ($>180^\circ\text{C}$), Fournier 1981, it is used in all phases and applied on spring and deep well samples.

$$t^\circ\text{C} = \frac{1217}{1.438 + \log(\text{Na}/\text{K})} - 273.15$$

Note: in the above equations, the Na and K concentrations are in mg/kg (ppm).

2.1.3 K-Mg geothermometers

This geothermometer was developed in the 1980's, and it was applied by Giggenbach, 1988. The basis for this geothermometer assumes that fluids have equilibrated with K-feldspar (adularia), K-mica (illite, muscovite), chlorite (clinochlore) and chalcedony (a silica phase which forms at slightly cooler temperatures than quartz):



The above are common hydrothermal minerals. In comparison to the Na-K geothermometers, this reaction equilibrates quickly over a range of temperatures from $<100^\circ$ to 300°C and hence it preserves cooler equilibration temperatures. Reliable temperatures are obtained in the application of this geothermometer to chloride waters only. Note that deeply derived chloride waters have Mg concentrations <1.0 ppm and that this geothermometer is very sensitive to $c_{\text{K}}^2/c_{\text{Mg}}$ ratios, any slight addition of Mg through mixing of shallow water with the deep fluid gives cooler temperatures.

K-Mg geothermometer, Giggenbach 1988, is used in all phases and applied in spring and deep well samples. The K and Mg concentration are expressed in mg/kg (ppm).

$$t^\circ\text{C} = \frac{4410}{14.0 + \log(\text{K}^2/\text{Mg})} - 273.15$$

2.1.4 Na-K-Ca Geothermometer

Historic information: Fournier and Trudell (1973) formulated this geothermometer to account for fluids containing relatively high calcium which give an anomalously high temperature using the Na-K geothermometer.

Considerations: This geothermometer is more complex as it was determined empirically from analyses of a large number of different fluids including geothermal and oil well waters. It assumes that fluid mineral equilibrium is established between Na and K feldspars, calcic minerals (calcium feldspar, epidote, calcite) and clay minerals. The following rules apply: first calculate the temperature using $\beta=4/3$, and cation concentrations expressed either as mg/kg or ppm. If that calculated temperature is $<100^\circ\text{C}$ and $[\log(c_{\text{Ca}}^{1/2}/c_{\text{Na}}) + 2.06]$ is positive, then this calculated temperature is appropriate. However, if the $\beta=4/3$

calculated temperature is $>100^{\circ}\text{C}$ or $[\log(c_{\text{Ca}}^{1/2}/c_{\text{Na}}) + 2.06]$ is negative, use $\beta=1/3$ to calculate the temperature. Obviously, the Na-K-Ca geothermometer is applicable to a larger range of thermal fluids than the Na/K geothermometer.

This geothermometer is affected by boiling and dilution. The main consequence of boiling is calcite (CaCO_3) precipitation which reduces the dissolved calcium concentration. A correction for fluids containing high concentrations of magnesium exists (Fournier and Potter, 1979; Giggenbach, 1988).

The equation of the geothermometer is:

$$t^{\circ}\text{C} = \frac{1647}{\log(\text{Na}/\text{K}) + \beta \log(\sqrt{\text{Ca}/\text{Na}}) + 2.24} - 273.15$$

The Na-K and Ca concentrations are in mg/kg (ppm).

3. RESULTS

Various geothermometers have been used in Costa Rica to try to estimate the temperature in the reservoir at the stage of exploration or to estimate the temperature of the different aquifers found in deep wells in both the development and exploitation phases. The geochemistry group must take into account some considerations when they apply the geothermometers:

- 1) Not all thermal spring waters are applicable by geothermometers, usually they are applied on hot springs, with high concentrations of chloride and if it is possible with a good flow rate.
- 2) The sampling and data collection must be accurate and reliable and must follow the standard procedures.
- 3) The sample analysis must be performed carefully, and the ionic balance for these samples must be less than $\pm 5\%$.

Some characteristics of the chloride springs found in the Costa Rican geothermal areas are mentioned in Table 1.

TABLE 1 Characteristics of the chloride springs, Costa Rica

Name	Code	Geothermal area	Temperature range ($^{\circ}\text{C}$)	Flow rate	Type
Salitral Bagaces	SB	Miravalles	60-65	Low	Chloride
Salitral Canas 1	SC 1	Tenorio	40-45	too low	Chloride
Salitral Canas 2	SC2		50-55	low	Chloride
Salitral Canas 3	SC3		55-60	low	Chloride
Luisan	LC		55-60	too low	Chloride
Salitral Norte 1	SN1	Rincón de la Vieja	70-75	High	Chloride
Salitral Norte 2	SN2		70-75	High	Chloride
Salitral Norte 3	SN3		low	Chloride	
Quebrada Huacas 1	QH1	Orosi	60-65	low	Chloride
Quebrada Huacas 2	QH2		60-65	low	Chloride
Quebrada Huacas 3	QH3		55-60	low	Chloride
Finca German V	PSN-4	Poco Sol	95-98	medium	Chloride
Finca Ivo Corral	PSN-7		55-60	medium	Chloride
Sitio Presa	PSN-13		70-75	medium	Chloride

In Costa Rica, the presence of such springs is scarce; almost all are medium temperature and low to medium flow rate. Only one (PSN-4) has a high temperature close to the boiling point and two (SN-1 and SN-2) have a high flow rate around 60 l/s.

On the other hand, the temperatures estimated using different geothermometers like Na-K of Fournier, Truesdell, Giggenbach and Arnórsson; Na-K-Ca of Fournier-Trusdell; Quartz maximum steam loss of Fournier applied to some samples of chloride waters are shown in the Table 2.

TABLE 2 Spring temperatures calculated using different geothermometers, Costa Rica

Ubicación	Na-K				Na-K-Ca	Quartz
	Four.	Trus.	Gigg.	Arnór.	F-T	msl
SB	141	97	160	128	155	146
SN1	209	178	225	194	198	136
SN2	208	177	224	193	198	134
SC1	120	73	140	109	138	153
LC	120	73	140	109	143	145
QH	136	92	156	123	146	152
PS4	200	167	217	185	194	171
PS13	199	165	215	183	183	147
PS7	201	168	217	185	182	135
QH	137	92	156	124	136	131
RCh	240	217	253	226	206	106
CU	112	65	133	102	111	134

The results indicate that the reservoir temperatures are low and these suggest that the reservoir could be a medium or low enthalpy field. The interpretation of these data should be done carefully and should take in account the characteristics of the terrain and the processes that can occur during the movement from the deep reservoir to the surface. Costa Rica has a steep topography and the fluids normally move slowly and carry long distances due to the topography of the land and that makes difficult the interpretation of the geothermometer data, because during the ascent the chemical composition may be affected by:

- Conductive heat loss: as the fluids travel through cooler rocks they become cool and probably the water changes their degree saturation with respect to primary and secondary minerals; and also bring some modifications in the chemical composition by mineral dissolution or precipitation. Usually that occurs if the travel time is long, allowing the re-equilibration fluid, then the temperature suggested by the geothermometer is from the last equilibrium and not from the deep reservoir as occurred with Salitral Bagaces located 20 km to the south of the Miravalles geothermal field, or Salitral Cañas located 25 km from the Tenorio geothermal area
- Boiling due to decreasing hydrostatic head and invariably causes changes in the composition of the rising fluid due to steam loss and the same process mentioned before can be occur.
- Mixing with cool groundwater is common in this type of terrain and occurs with the samples from Salitral Bagaces and Salitral Norte. The sample of the POCO Sol area is less affected by this process.

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