Proceedings World Geothermal Congress 2010
Bali, Indonesia, 25-29 April 2010

# Fluid-Mineral Equilibrium of Spring Waters at Cuitzeo Basin (Mexico) Geothermal Zone

Nuria Segovia[1], Rosa María Barragán[2], Ruth Alfaro[3], Víctor M. Arellano[2], Manuel Mena[1]

[1]Universidad Nacional Autónoma de México, Instituto de Geofísica, Circuito Exterior, 04510 México, D. F.

nurina@terra.com.mx

[2] Instituto de Investigaciones Eléctricas, Gerencia de Geotermia, Reforma 113, Col Palmira, 62490 Cuernavaca, Mor, México

[3]Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mich., México

**Keywords:** fluid-mineral equilibrium, reservoir temperature, saturation indices, Cuitzeo Basin, Mexico, geothermal springs

## ABSTRACT

In this work fluid-mineral equilibrium for six spring waters from Cuitzeo Basin geothermal zone for a range of temperatures was studied in order to investigate the temperature/s at which it was attained and by this approach, to estimate the reservoir temperature. The results of both the chemical speciation and the saturation indices of hydrothermal minerals were obtained from the chemical composition of spring waters as input data by using the REACT routine of the Geochemist Workbench (GWB) program for a wide range of temperatures (from sampling temperature to 300°C). Suitable plots of saturation indices vs temperature were developed by using the GTPLOT routine of GWB. As an example, the results for one spring with a sampling temperature of 75°C are given. For this sample the fluid-mineral equilibrium results indicated not only one temperature since saturation indices of some minerals tended to converge each other at the cero value at 240-260°C; 180-200°C and 140-150°C. These results partially agreed with reservoir temperature estimations obtained by chemical geothermometers which provided the following results: T Na/K between 132 and 146°C and T $SiO_2$ between 188 and 194°C (depending on the expression used). As no chemical geothermometers provided temperatures as high as 250°C for the reservoir, it is suggested that cooling processes of the original fluid take place by mixing with shallower, lower temperature waters when the fluid flows to the surface. These results are useful to support exploration and development activities at Cuitzeo Basin zone to make use of the resources for power generation and/or direct applications.

## 1. INTRODUCTION

Cuitzeo lake is located in the northern part of Michoacan state (Mexico), (100º 39'- 101º 20' W and 19º 46'- 19º 59' N) at an average altitude of 1850 m (Figure 1). Geochemical and radon data interpretation of sixteen sites at Cuitzeo lake where springs occur, were documented by (Segovia et al, 2005). In the results, relatively large differences in reservoir temperature estimations were observed when using different geothermometers. In general, these differences were attributed to cooling processes occurring during the ascent of fluids to the surface, which also affect the response of geothermometers depending on the re-equilibration rate of every expression. In order to avoid some of the basic assumptions of each specific geothermometer, including that related to the type of minerals with which the fluid has attained equilibrium, the approach based on the saturated state of hydrothermal minerals allows the temperature estimation to be obtained (Reed and Spycher, 1984; Bethke, 1996). The objective of this work was the modeling of fluid-mineral equilibria for springs from the Cuitzeo Basin zone, in order to estimate the reservoir temperatures through the saturation indices of hydrothermal minerals.

## 2. METHODOLOGY

Data from Cuitzeo, San Agustin del Pulque, San Juan Tararameo, San Agustin del Maiz, and Araro (Figure 1; Table 1) (Segovia et al, 2005; Herrera et al, 2009) were used.

Fluid-mineral equilibrium modeling was accomplished by using the program REACT of the Geochemist Workbench package (GWB) (Bethke, 1996) for a wide range of temperatures in order to obtain the saturation indices of hydrothermal minerals. Subsequently the saturation indices were plotted against the temperature by using the GTPLOT program of the GWB software to investigate at which temperatures such indices tend to converge each other to zero, indicating that fluid-mineral equilibrium was attained at such temperature.

## 3. CHEMICAL MODELING

### 3.1 Ion Association and Ion Interaction Models

Aqueous solution models are widely used to calculate the in situ equilibrium thermodynamic characteristics of a solution under a given set of conditions (temperature, pressure, etc) based on measured total composition (Truesdell et al, 1987). The estimated thermodynamic characteristics include ion activities (including pH), gas partial pressures or fugacities and the state of saturation of the fluid regarding mineral phases. The accuracy of the model is mainly affected by the quality and completeness of the thermodynamic data and by the appropriateness of the model used for activity calculations. The ion association model assumes the existence of ion-pairs and uses activity coefficients that depend on total concentration but are assumed to be independent of the specific solution involved. In contrast, the ion interaction model describes experimental results in terms of interaction coefficients between ions that are specific to the ion combinations studied and cannot be generalized unless all possible combinations have been studied. These interaction coefficients cannot be extrapolated to other temperatures, unlike the ion association model that uses equilibrium constants and activity coefficient expressions that are functions of temperature. The solutions with concentrations less than one molal (about 60,000 mg/kg NaCl) can be modeled using the ion association models.

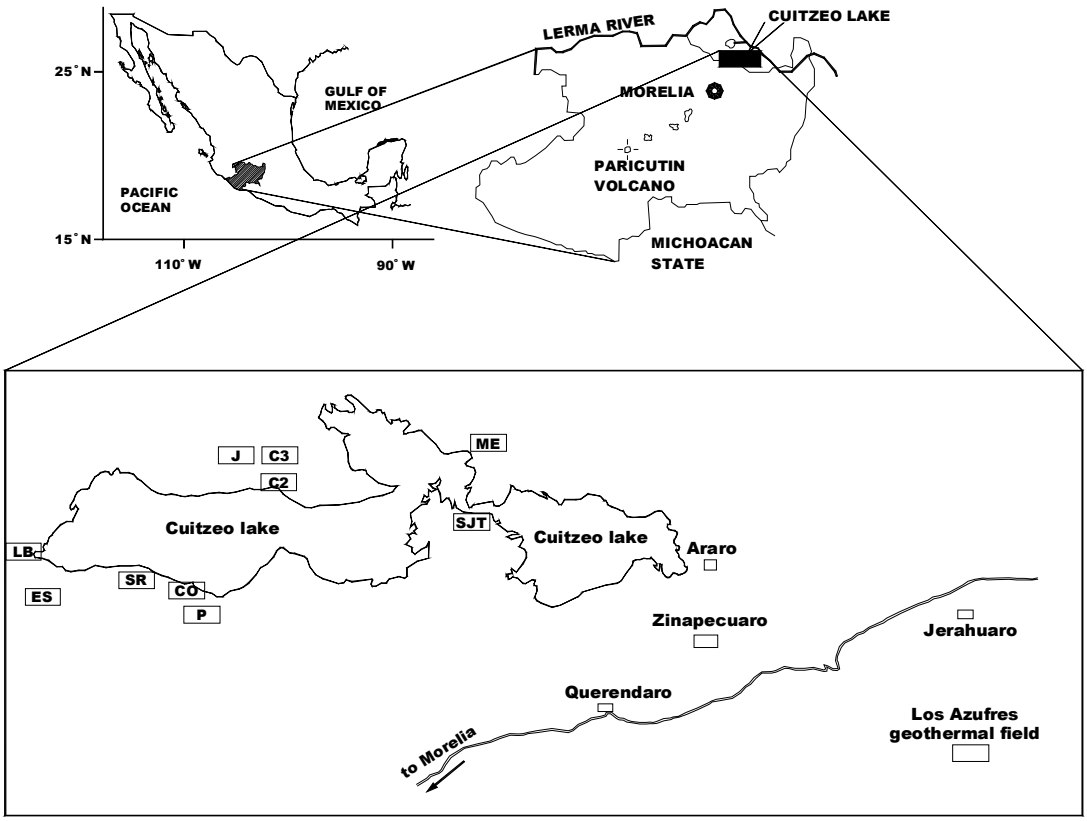


**Figure 1: Location of Cuitzeo lake including several studied sites (Segovia et al, 2005).**

**Table 1. Chemical composition of the studied samples. Concentrations in mg/kg, sampling temperature in ºC (Segovia et al, 2005; Herrera et al, 2009).**

| SITE | CODE | T (°C) | pH | Na | K | Ca | Mg | $HCO_3$ | $SO_4$ | Cl | B | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CUITZEO 2 | C2 | 26.5 | 8.4 | 56.2 | 14.1 | 37.5 | 37.67 | 372.8 | 41.3 | 8.0 | 0.2 | 67.5 |
| SAN AGUSTIN DEL PULQUE | SAP | 75.0 | 8.0 | 406.0 | 11.0 | 33.0 | 0.20 | 262.0 | 591.0 | 95.8 | 3.0 | 241.0 |
| SAN JUAN TARARAMEO 3 | SJT-3 | 82.0 | 8.9 | 774.0 | 30.0 | 1.0 | 0.28 | 525.0 | 947.0 | 280.0 | 4.6 | 270.0 |
| SAN AGUSTIN DEL MAIZ | SAM | 89.0 | 7.3 | 542.0 | 27.0 | 14.2 | 0.40 | 623.0 | 591.0 | 130.0 | 3.9 | 250.0 |
| ARARO 1 | AR-1 | 60.0 | 7.8 | 691.3 | 55.5 | 26.5 | 0.50 | 134.0 | 138.8 | 1046.8 | 65.2 | 134.0 |
| ARARO 2 | AR-2 | 60.0 | 7.7 | 756.5 | 60.6 | 32.6 | 0.50 | 158.5 | 153.6 | 1290.2 | 80.4 | 257.5 |

**Table 2. Reservoir temperatures (ºC) estimated by different geothermometers (Segovia et al, 2005).**

| CODE | T Na-K-Ca (Fournier and Truesdell, 1973) | T Na/K (Nieva and Nieva, 1987) | T $SiO_2$ (Fournier and Potter II, 1982) | T $SiO_2$ (Giggenbach, 1992) |
|---|---|---|---|---|
| C2 | 89 | 38 | 116 | 95 |
| SAP | 125 | 132 | 194 | 188 |
| SJT-3 | 181 | 136 | 202 | 199 |
| SAM | 167 | 152 | 197 | 192 |
| AR-1 | 192 | 186 | 156 | 140 |
| AR-2 | 191 | 186 | 199 | 194 |

### 3.2 Data and Activity Coefficients

The thermodynamic data used in a solution model consists of a set of equilibrium constants that are used in equilibrium expressions to describe the stability of an ion, gas or mineral in terms of the concentrations and activity coefficients of other ions. Thus, there is one equilibrium expression for each secondary ion (i. e., for $NaSO_4^-$ but not for $Na^+$ or $SO4^{=}$) that relates its concentration to those of a set of primary ions. For each element there is also a mass

balance equation and for the entire solution a charge balance equation. These equations together with activity coefficients are enough to allow the calculation of activities of all the species in solution including pH. After the solution model has been calculated, the derived concentrations and activity coefficients may be combined into another set of equilibrium expressions to calculate equilibrium quotients (Q) describing the solution of minerals. These equilibrium quotients are then compared with appropriate equilibrium constants (K) to indicate whether the solution is undersaturated, saturated or supersaturated with each mineral. This comparison is usually expressed as values of log (Q/K) with zero indicating exact saturation.

### 3.3 The GWB software

At present many computer programs are available to perform chemical equilibrium modeling for geothermal fluids, some of them are specially suited for geothermal wells data, i. e. ENTHALP (Truesdell and Singers, 1976); WATCH (Arnórsson et al, 1982); EQ3/EQ6 (Wolery, 1983); EQQYAC (Barragán and Nieva, 1989) among others. The GWB software (Bethke, 1996) was developed for a more general geological purposes, it includes the REACT program that calculates chemical speciation of the fluid for a given temperatures and also the saturation indices of hydrothermal minerals. Activity coefficients were calculated by using an extended form of the Debye-Hückel equation as the ionic strength of spring fluids is very low. Thermodynamic database of GWB was created at Lawrence Livermore National Laboratory. The results are usually plotted by the program GTPLOT included in GWB software.

## 4. RESULTS

The results of saturation indices of some minerals vs temperature for the San Juan Tararameo site (SJT-3 sample), with a sampling temperature of 80°C are given in Figure 3. As seen in the figure, intersections at zero value for the saturation indices of common hydrothermal minerals occur at about 155°C; 175-180°C and 200°C. As there is not a single intercept with the zero value line, more than one fluid-mineral equilibrium was attained, due probably to cooling processes occurred during fluid up-flowing to the surface. These results partially agreed with results from chemical geothermometers (Table 2) as follows. The Na/K (Nieva and Nieva 1987) geothermometer provided 136°C; the Na-K-Ca geothermometer (Fournier and Truesdell, 1973) gave 181°C while silica geothermometers estimations were 202°C by using the expression given by Fournier and Potter II, (1982) and 199°C by using the expression given by Giggenbach, (1992) as most suitable for hot springs data. The intersection of the phase chalcedony line with the zero value line is seen at about 155°C; while that for the phase quartz occurs at about 200°C.

The saturation indices obtained for the San Agustin del Pulque sample (SAP) vs temperature, which has a sampling temperature of 75°C, are given in Figure 4.

As in the case of the SJT-3 sample, there are more than one interception of the saturation indices curves with the zero line, which occur at about 140°C, 175°C, 200°C and 220°C. The geothermometers for this sample provided the following temperatures (Table 2). Na-K-Ca: 125°C; Na/K: 132°C and silica (quartz) (Fournier and Potter II, 1982): 194°C while silica (Giggenbach, 1992): 188°C. According to the silica-enthalpy mixing model obtained for Cuitzeo samples, both springs (SJT-3 and SAP) resulted from the mixing of a hot component at a temperature of about 220°C with relatively shallow waters in a proportion of about 50% (Segovia et al, 2005).

In Figures 5 and 6 the saturation indices of some hydrothermal minerals in springs from Araro site (AR-1 and AR-2 samples) vs temperature were plotted. As seen in figures, there is not a single interception of the saturation lines with the zero line. According to Figure 5 crosses of saturation lines occur along a relatively wide range of temperatures, from About 130 to 160°C, where quartz attained equilibrium while "older" equilibrium is noticed at 185°C by saturation lines (of quartz, anhydrite and albite) interceptions located below the zero line.

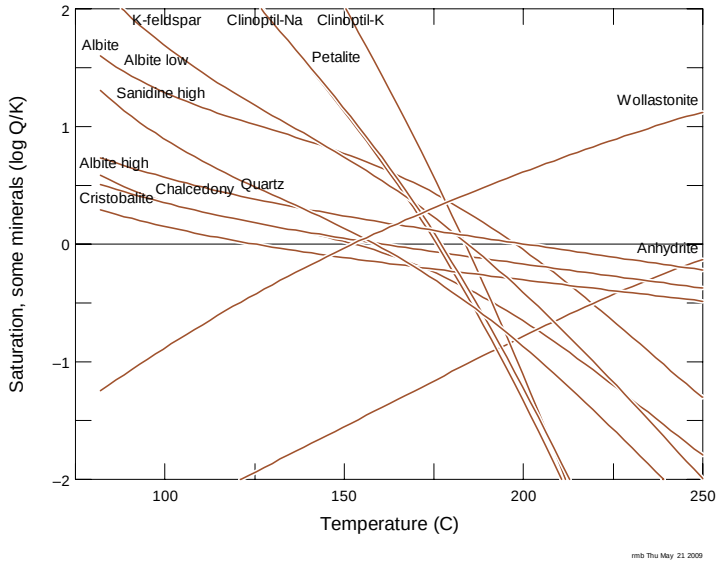


**Figure 3: Saturation indices of some hydrothermal minerals vs temperature for the San Juan Tararameo (SJT-3) spring.**

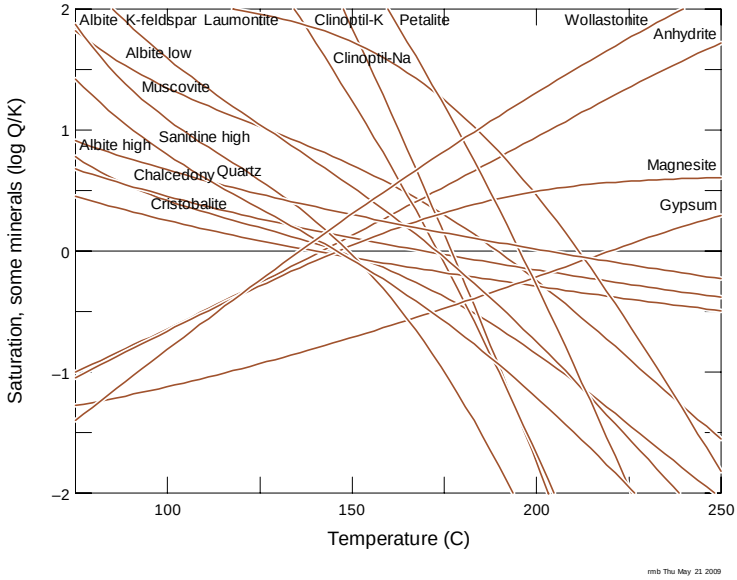


**Figure 4: Saturation indices of some hydrothermal minerals vs temperature for the San Agustin del Pulque (SAP) spring.**

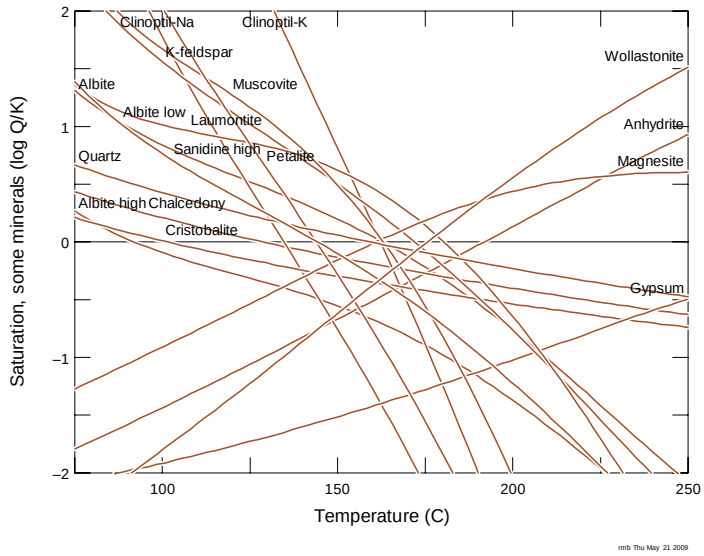


**Figure 5: Saturation indices of some hydrothermal minerals vs temperature for the Araro (AR-1) spring.**

In Figure 6 the interceptions of the saturation lines of the AR-2 sample with the zero saturation value line are seen at higher temperatures, regarding these observed for the sample AR-1. For sample AR-2 the temperature range is found between 175 and 210°C while most of the crosses occur at 185°C. For both the samples the cationic geothermometers provided the same temperatures as follows. Na-K-Ca expression provided 190°C while Na/K expression 186°C.

The silica geothermometers obtained for AR-1 sample (Table 2) were 156°C according to Fournier and Potter expression and 140°C by using the Giggenbach's expression. In contrast for the AR-2 sample silica geothermometers provided 199°C and 194°C utilizing both geothermometers respectively. According to the silica-enthalpy model results (Segovia et al, 2005), both samples resulted from the general mixing process between basically two fluids proposed, as explained for the SJT-3 and SAP samples. For the AR-2 sample a similar amount of hot component than that found for samples SJT-3 and SAP of 50% was estimated, while in the AR-1 sample because of higher dilution regarding AR-2, the contents of hot fluid was about 20%.

In Figure 7 the saturation indices lines for the San Agustin del Maiz site (SAM sample) which showed the maximum sampling temperature (89°C), vs temperature are given.

As in the previous cases studied, in Figure 7 a range of equilibrium temperatures is observed through the behavior of the saturation lines as they intercept the zero saturation line. Important crosses occur at 170°C where chalcedony attains equilibrium and also at 210°C where quartz is equilibrated. Geothermometer results for this sample were as follows (Table 2). Na-K-Ca: 167°C; Na/K: 152°C; while silica expressions provided 197°C and 192°C by using the Fournier and Potter and the Giggenbach expressions, respectively. As seen in Figure 7, the cristobalite and the paragonita lines approach the zero saturation line at the temperature given by the Na/K geothermometer while the "older" equilibrium given by the interception of saturation lines for quartz, barite and clinoptil-Ca below the zero saturation line indicates fluid-mineral equilibrium attainment at about 250°C. This temperature is higher than that obtained from the silica –enthalpy model (220°C) for the hotter component and are likely to occur around San Agustín del Maiz site.

In order to define the equilibrium characteristics of the shallower waters participating in the mixing process at Cuitzeo Basin, the sample Cuitzeo-2 with a sampling temperature of 26.5°C was taken as representative for modeling. The saturation indices of some minerals including silica phases vs temperature for this sample are given in Figure 8 while saturation indices of Al-bearing minerals are shown in Figure 9.

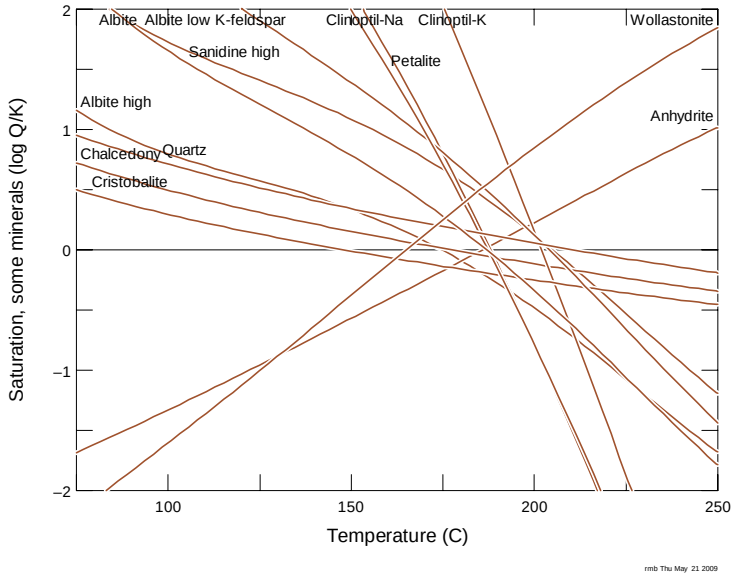


**Figure 6: Saturation indices of some hydrothermal minerals vs temperature for the Araro (AR-2) spring.**

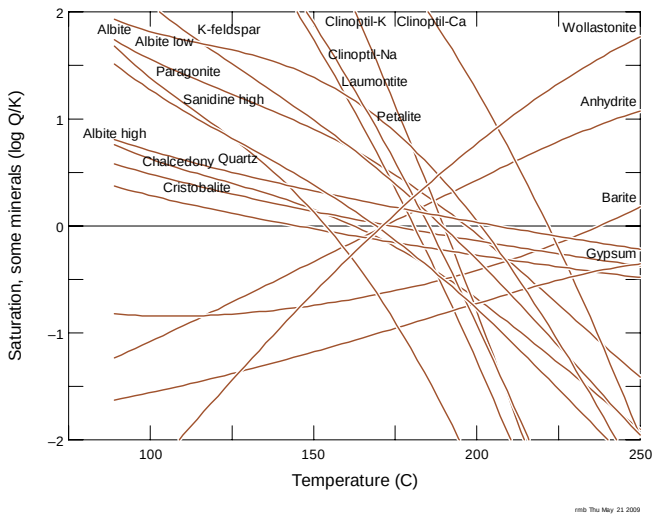


**Figure 7: Saturation indices of some hydrothermal minerals vs temperature for the San Agustín del Maiz (SAM) spring.**

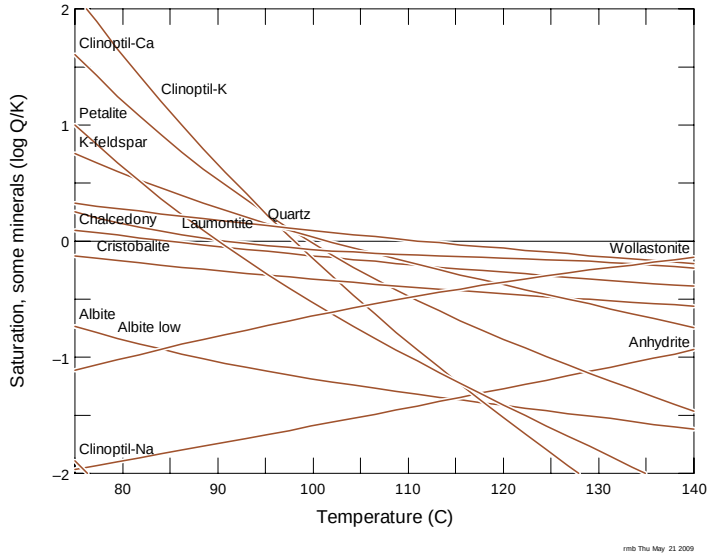


**Figure 8: Saturation indices of some hydrothermal minerals including silica phases vs temperature for the Cuitzeo-2 (C-2) spring.**

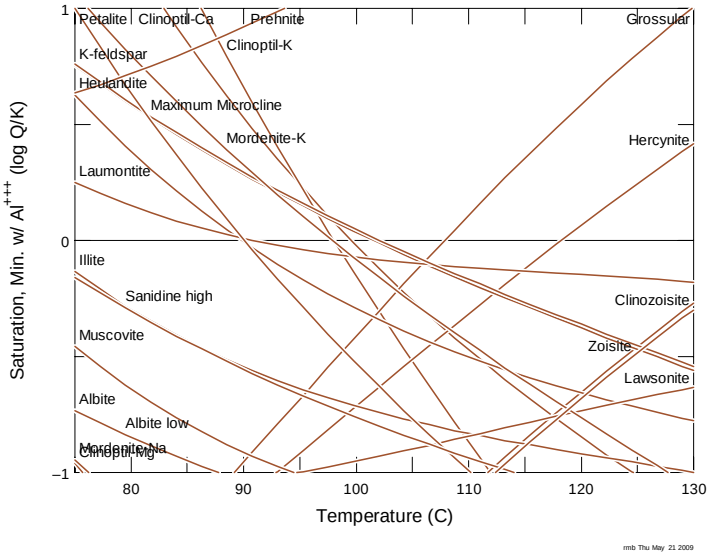


**Figure 9: Saturation indices of Al-bearing hydrothermal minerals vs temperature for the Cuitzeo-2 (C-2) spring.**

For this sample very low Na/K temperature was estimated by using the Nieva and Nieva (1987) expression (38°C), (Table 2) which is attributed to the relatively high Mg concentration of the sample regarding the concentrations of Na, K and Ca. In contrast, the Na-K-Ca temperature provided 89°C, which is very close to the interception of the saturation line of chalcedony in Figure 8 and some other Al-bearing minerals in Figure 9. The saturation line for quartz intercepts the zero saturation line in Figure 8 at about 110°C, while Al-bearing minerals show a range of equilibrium temperatures between 100°C and 103°C and an "older" equilibration at about 105°C, where grossular and laumontite saturation lines among these for other minerals converged each other, slightly below the zero saturation line. These results suggest that Cuitzeo-2 sample has a relatively low content of hot component and that cooling processes like mixing when fluid up-flows to the surface are occurring at the system. However in spite of the relatively poor content of hot fluid in this sample, minimum reservoir temperatures of about 90-100°C could occur, which are suitable for many direct applications.

## 5. CONCLUSIONS

The fluid-mineral equilibrium modeling for a wide range of temperatures of Cuitzeo Basin samples provided the saturation indices of characteristic hydrothermal minerals.

The results allowed to explain the differences obtained in reservoir temperatures estimations by using different geothermometers. The results supported the occurrence of mixing between basically two fluids, in different proportions, to produce the springs chemistry observed at the surface. At one of the sites maximum reservoir temperatures of about 220-250°C are likely to occur while according to results of the less saline samples at the system minimum temperatures could be of about 90-100 °C. As no temperatures as high as 250°C were estimated by using geothermometers, it is suggested that cooling processes of the original fluid take place by mixing with shallower, lower temperature waters when the fluid flows to the surface.

**REFERENCES**

Arnórsson, S., Sigurdsson, S. and Svavarsson H.: The Chemistry of Geothermal Waters in Iceland I. Calculation of Aqueous Speciation from 0 to 370°C, Geochimica et Cosmochimica Acta, 46, (1982), 1513-1532.

Barragán, R. M. and Nieva, D.: EQQYAC: Program for Determining Geothermal Reservoir Chemical Equilibrium, Computers and Geosciences, 15, (1989), 1221-1240.

Bethke, C. M.: Geochemical Reaction Modelling, Concepts and Applications, Oxford University Press, (1996).

Fournier, R. O., Truesdell, A. H.: An Empirical Na-K-Ca Geothermometer for Natural Waters, Geochimica et Cosmochimica Acta, 43, (1973), 1543-1550.

Fournier, R. O., Potter II, R. W.: A Revised and Expanded Silica (Quartz) Geothermometer, Geothermal Resources Council Bulletin, November, (1982), 3-12.

Giggenbach, W.F.: Chemical Techniques in Geothermal Exploration, In: Proceedings, F. D'Amore (Editor), Applications of Geochemistry in Geothermal Reservoir Development. UNITAR/UNDP, Rome, (1992), 119-144.

Herrera, M. A., Alfaro, R., Segovia, N., Cortés, R. and Villalobos B.: Determination of Heavy Metals and Arsenic in Water and Soil Samples of Cuitzeo Lake. Manuscript submitted to Water Air and Soil Pollution, (2009).

Nieva, D. and Nieva, R.: Developments in Geothermal Energy in Mexico-Part Twelve. A Cationic Geothermometer for Prospecting of Geothermal Resources, Heat Recovery Systems & CHP, 7, (1987), 243-258.

Reed, M. and Spycher, N.: Calculation of pH and Mineral Equilibria in Hydrothermal Waters with Application to Geothermometry and Studies of Boiling and Dilution, Geochimica et Cosmochimica Acta, 48, (1984), 1479-1492.

Segovia, N., Barragán, R. M., Tello, E., Alfaro, R. and Mena, M: Geochemical Characteristics and 222Rn Measurements at Cuitzeo Basin (Mexico) Thermal Springs and Artesian Wells, Proceedings, World Geothermal Congress, Antalya, Turkey, (2005).

Truesdell, A. H. and Singers, W.: The Calculation of Aquifer Chemistry in Hot-water Geothermal Systems, U. S. Geological Survey, Jour. Research, 2, (1976), 271-278.

Truesdell, A. H., Winnett, T. L., Nieva, D., Barragán, R. M. and Ramírez, E.: Chemical Modeling of Geothermal Aquifer Fluids with Sample Calculations for Los Azufres and Cerro Prieto, Proceedings, International Symposium on development and Exploitation of Geothermal Resources, Cuernavaca, Morelos, Mexico, October 5-9 (1987), 194-201.

Wolery, T. J.: EQ3NR: A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations, Report, UCRL 53414, Lawrence Livermore Nat. Lab., (1983).