

REVISED QUARTZ SOLUBILITY TEMPERATURE DEPENDENCE EQUATION ALONG THE WATER-VAPOR SATURATION CURVE

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Key words: chemical thermodynamics, quartz solubility, PVT characteristics of water, regression equation, quartz geothermometer, Cerro-Prieto.

ABSTRACT

From the application of chemical thermodynamics a quartz solubility regression expression along the water-vapor saturation curve for whole range of temperature from 0 to 374°C was developed. The equation is the following

$$\log SiO_2(ppm) = -\frac{1175.7(\pm 31.7)}{T(K)} + 4.88(\pm 0.08)$$

The correction of total discharge silica composition from a well for the vapor fraction in the geothermal reservoir is a fundamental limitation to use this equation as a geothermometer. For knowing the vapor fraction there is indirectly need of knowing the reservoir temperature. It is possible to calculate the deep reservoir temperature with iteration process, but a basic assumption is that the reservoir fluid is in equilibrium with quartz. The concept is elucidated in case of the Cerro Prieto geothermal system.

1. INTRODUCTION

The use of silica content as a geothermometer is presently an integral part of almost all the geochemical investigations of geothermal systems around the world. The derivation of such geothermometers is basically based on the regression of experimental solubility data. White et al. (1956) found first that the silica content could be used as a geochemical indicator of geothermal reservoir temperature, as the silica concentration in hot springs at Steamboat, Nevada was very close to the experimental solubility of amorphous silica. Since then enormous contributions have been made to gather more field evidences and to create a systematic approach to understand the geothermal reservoir characteristics from the fluid geochemistry of silica. Mahon (1966) showed that the concentration of silica in hot water discharged from drillholes at Wairakei in New Zealand is in agreement with solubility of quartz after corrections for adiabatic steam loss. From the experimental quartz solubility data Fournier (1977) presented the first geothermometer in equation form. Henley et al. (1984) compiled all the existing silica geothermometers for many silica phases, including the effects of adiabatic and conductive cooling processes. Fournier and Potter (1982) derived a polynomial equation for the quartz geothermometer using the revised quartz solubility data, which is applicable up to 330°C. Verma and Sontoyo (1997) applied a statistical data treatment method and theory of error propagation in improving this silica geothermometer equation. They had to eliminate the data points for temperature higher than 300°C as those points were outlier according to their statistical analysis.

Recently, Rimstidt (1997) compiled all the quartz solubility data along the water-vapor saturation curve and derived a regression expression that is valid up to 300°C. In many geothermal fields the reservoir temperatures have been measured above than 300°C. Therefore, it is necessary to know the quartz solubility data at temperatures higher than 300°C in order to deal the geochemistry of high temperature hydrothermal systems.

Verma (1999) presented the chemical thermodynamic calculations for quartz solubility for a wide range of temperature and amount of water in the reaction vessel. It was observed a wide difference between calculated and experimental solubility. With a critical evaluation of this discrepancy he concluded a need of creating internal consistent thermodynamic data for aqueous silicic species and reevaluation of quartz solubility data at higher temperatures along the water-vapor saturation curve.

In this article the chemical thermodynamic concepts are used to understand the causes of decrease in the quartz solubility after 300°C along the water-vapor saturation curve in the existing data in literature. Similarly a combined evaluation of the quartz solubility data along the water-vapor saturation curve and in the compressed liquid region is presented in order to derive a quartz solubility regression expression along the water-vapor saturation for whole range of temperature (0-374°C). The limitations for using this expression as a geothermometer is discussed considering the well CP-M-19A at Cerro Prieto as an example.

2. EXPERIMENTAL QUARTZ SOLUBILITY DATA

In the solubility determination experiments, a certain amount of water and silica is closed in a reaction vessel (or bomb) and the system is heated to a certain temperature. Let us assume that there is only pure water in the vessel in order to understand the effects of heating on the thermodynamic state of such systems. Figure 1 shows the PT relations for water along different isochores. These curves have been constructed with using the steam tables of Haar et al. (1984). For the cases when the total specific volume (i.e. the total volume of container divided by the total weight (mass) of water and vapor) is greater than the critical specific volume of water (3.106 cm³/g), there is only vapor at a certain high temperature and vice versa (Verma, 1997). On the other hand, if the total specific volume of water is just equal to the critical volume of water, there will be water and vapor along the water-vapor saturation curve up to the critical point. After the critical point there will not be any distinction between water and vapor along the V=3.106 cm³/g line, but there will be compressed liquid at any point above this line and superheated steam below it even in the supercritical region. Therefore there are two extreme cases for conducting solubility determination

experiments when there will always be water in the reaction vessel at high temperature: i. the vessel is just filled equal to the critical volume of water ($V=3.106 \text{ cm}^3/\text{g}$) and ii. the vessel is completely filled at the initial room temperature ($V=1.00 \text{ cm}^3/\text{g}$). And there could be any proportion of water and vapor along the saturation curve.

All the quartz solubility data from literature are divided in two groups: a) along the water-vapor saturation curve (compiled data from Rimstidt, 1997 and Verma, 1999) and b) in the compressed liquid region (Compiled data from Verma, 1999). Let us first analyze the quartz solubility along the water-vapor saturation curve. In very early works the quartz solubility at room temperature (25°C and 1 bar) is reported as 12 ppm (Brisco et al., 1936-7; van Lier et al., 1960). Fournier and Potter (1982) and Fleming and Crerar (1982) accepted the value 6.6 ± 1 ppm. But recently Rimstidt (1997) conducted the solubility determination experiments for a long period and got the value of 11.0 ± 1.1 ppm. To attain equilibrium between water and quartz at room temperature requires doing experiments for geological time period without supersaturating the solution at any instant, to prevent equilibrium with other silica phases. If all the limitations involved in the quartz solubility determinations are considered, it is justifiable considering all the above values within analytical errors (Gerardo-Abaya et al., 1997).

Figure 2 shows the temperature dependence of quartz solubility along the water-vapor saturation curve. Rimstidt (1997) critically analyzed the solubility data and fitted the regression expression up to 300°C . He did not consider the quartz solubility data from Fournier and Potter (1982), because those data were obtained by regression. He himself measured quartz solubility at four temperatures 21, 50, 74, and 96°C , but he considered ten values for his quartz solubility regression: 2 for 21, 2 for 50, 2 for 74 and 4 for 96°C . Similarly he also took repeated values of silica solubility by other authors from literature (Siever, 1962; Crerar and Anderson, 1971). Therefore, the solubility data are refitted here removing the duplicated values given by the same author (Figure 3). The refitted expression is more or less same as proposed by Rimstidt; but it is more realistic, because it avoids a biased statistical evaluation of the dataset due to repetition of data points. Here I have included all the existing values of quartz solubility at 25°C between 6.6 to 12 ppm. The errors in the coefficients of the following regression equation are only the statistical errors of $\pm 1 \sigma$ (standard deviation).

$$\log \text{SiO}_2 (\text{ppm}) = -\frac{1175.7(\pm 31.7)}{T(\text{K})} + 4.88(\pm 0.08)$$

The error in the coefficients is higher than that reported by Rimstidt (1997). It is due to the fact that the less number of reliable data points are considered here.

The decrease in the existing quartz solubility data along the water-vapor saturation curve after 300°C in the Figure 2 can be explained taking into account the PVT characteristics of water and the details on the solubility measurement techniques. As mentioned above, at a specified temperature or pressure along the water-vapor saturation curve, there could be any amount of vapor from 0 to 100%. The specific volume of vapor at low temperatures is very high; therefore the volume of vapor doesn't affect significantly the solubility of any mineral like

quartz, which is only soluble in the liquid phase. But at higher temperatures (above 300°C) it does affect as the specific volumes of water and vapor are of same order of magnitude. Most of the quartz solubility determinations were performed with the weight loss method or by rapid quenching of reaction vessel to room temperature. In both the cases the solution after quenching has condensed vapor which indirectly modifies (rather decreases) the concentration of silica in the solution. Therefore, knowledge of proportion of water and vapor is vital to solubility determination along the saturation curve at temperatures higher than 300°C . Unfortunately, it has been ignored in the quartz solubility determinations in the literature.

Under these circumstances a combined evaluation of quartz solubility data along the water-vapor saturation curve and in the compressed liquid region will be helpful in understanding the behavior of quartz solubility data above 300°C (Figure 2). The values of pressure and temperature for all the solubility experiments in the compressed liquid region together with the theoretical PT curves for the two above mentioned extreme cases are plotted in Figure 4. All the experimental pressure and temperature data lie between the theoretical curves. Therefore the pressure and temperature during all these solubility studies were probably controlled by the different amount of water in the reaction vessel. Thus the quartz solubility data of the points, which are near to the saturation curve and the extended line in the supercritical region in the Figure 4, could define the tendency of the solubility data along saturation curve after 300°C .

In the Figure 2 the solubility regression expression is also plotted with extrapolation up to 400°C . It can be observed in the figures 4 and 2 that there are clusters of compressed liquid solubility data points near to the saturation curve and to the regression expression in the temperature range $300\text{--}400^\circ\text{C}$, respectively. Additionally, there is no decrease in the silica solubility values for the compressed liquid region with temperature. Theoretically, there should not be any solubility data point for the compressed liquid region on the lower side of the regression expression. Apart from all these limitations it can be concluded that the extrapolation of the regression expression to higher temperatures is valid and the existing quartz solubility data along the water-vapor saturation curve are needed to be revised after 300°C . Therefore in the absence of accurate data above 300°C along the water-vapor saturation curve the extrapolation of the low temperature regression expression is a better option for interpreting silica chemistry in the natural high temperature hydrothermal systems.

3. CRITIQUE ON SILICA GEOTHERMOMETER

The silica geothermometer has been applied extensively to estimate the geothermal reservoir temperature from the silica concentration of fluids obtained from natural manifestations and drilled wells. Unfortunately, the predicted temperatures generally show a wide dispersion even when applying a single geothermometer to all the wells in a geothermal field. Many reasons have been proposed to justify the discrepancies, including gain or loss of steam phase in the reservoir, mixing of different types of fluids, re-equilibration during ascension to surficials, precipitation-dissolution, etc. (Truesdell and Fournier, 1977).

There could always be some silica concentration data points which satisfy a given geothermometer equation. Thus it is not a proper approach to validate some geothermometer equation through application to some specific dataset. In the case of silica there is still a deficiency in the experimental and theoretical information needed to understand geological processes through its fluid chemistry (Verma, 1999). Secondly, it requires to justify independently that the deep reservoir fluid is in equilibrium with quartz.

Recently, Verma and Santoyo (1997) improved the silica geothermometer equation proposed by Fournier and Potter (1982) and applied their equation to demonstrate reasonable agreement between the estimated and measured reservoir temperatures in the Cerro Prieto geothermal reservoir. They took the chemical data for the reservoir liquid from Fausto et al. (1979). One way to calculate deep-liquid composition is by knowing reservoir enthalpy and temperature. Probably, Fausto et al. (1979) used the silica temperature for this purpose. They did not state clearly the procedure that they used for the reservoir fluid concentration calculation. In the same proceedings Truesdell et al. (1979) presented results indicating that the silica temperature in all the wells in Cerro Prieto were always lower than the measured, NaKCa and enthalpy temperatures.

Thus, till now, enormous works have been done on improving the silica geothermometer equation and its applications. But there is a fundamental question to be answered on the correction of silica total-discharge concentration for vapor fraction in the geothermal reservoir fluid in order to use silica content in geothermal fluids as a chemical geothermometer. Similarly, it is also needed to justify that the silica in equilibrium with the geothermal fluid is only in the form of quartz.

Verma (1997) presented a two-phase flow approach to calculate the fluid thermodynamic parameters including chemical speciation, pressure, and temperature in a geothermal reservoir from the parameters measured in the geothermal fluid (vapor and liquid) at the wellhead separator. Using this approach the geothermal reservoir fluid parameters were calculated in the well M-19A at Cerro Prieto. The concentration of silica is 666 ppm and the reservoir temperature is 248°C. The data point is shown in Figure 5. It can be observed that the value is higher than the experimental quartz solubility, but is lower than the thermodynamically calculated solubility. Thus the fluid is supersaturated with respect to quartz, if the experimental data are considered accurate.

Secondly, if, for example, we devise the silica geothermometers based on the three datasets for quartz solubility (i.e. using data from Fournier and Potter, 1982; regression expression developed in this study and the thermodynamically calculated by Verma, 1999) along the water-vapor saturation curve, the reservoir temperature obtained by these geothermometers for the well M-19A will be approximately 297, 299 and 235°C, respectively. Verma (1997) also calculated the vapor fraction in the reservoir as 0.244 by weight. Therefore the total discharge concentration of silica at the wellhead was 517 ppm (Figure 5). If we apply the above geothermometers on the total discharge concentration, the reservoir temperatures will be approximately 270, 265 and 220°C, respectively. Additionally, if the regression solubility

data of Fournier and Potter (1982) are considered correct, the temperatures could also be 364 and 372°C for reservoir and total discharge silica concentration, respectively (Figure 5).

It is clear that the dispersion in the calculated temperature values is higher than the errors reported in the experimental solubility data and in the thermodynamic dataset for this silica-water system. Secondly, the corresponding temperature values for the reservoir fluid and the total discharge concentration of silica have a difference of approximate 30°C in this case, when there is only 22.4% by weight vapor in the reservoir. As we have seen that there could be any amount of vapor from 0 to 100% along the water-vapor saturation curve. Therefore, the independent estimation of reservoir vapor fraction is essential in the application of silica geothermometry. The two-phase flow approach gives the values of vapor fraction and the temperature without using any empirical geothermometer equation (Verma, 1997). Therefore the silica solubility data could also be useful to understand the state of silica-water equilibrium.

Let us consider that the fluid is in equilibrium with quartz. The iteration process is shown in Table 1. It can be seen that the deep reservoir silica concentrations obtained by mass balance and the regression equation are same for 270°C. There will be only 1.1% by weight of vapor fraction in this case.

CONCLUSIONS

The quartz solubility regression expression is derived by a critical scrutiny of all the existing experimental data along the water-vapor saturation. The reported solubility data after 300°C are definitely incorrect as the proportion of water and vapor in the reaction vessel was not taken into account. A thermodynamic evaluation of all the quartz solubility data along the water-vapor saturation and in compressed liquid region justifies the extrapolation of the low-temperature solubility regression expression. Thus the present expression is valid for whole range of temperature from 0 to 374°C.

The unknown value of reservoir vapor fraction is a fundamental limitation in using the quartz solubility expression as a chemical geothermometer on the total discharge composition of a well. In case of the CP-M-19A well at Cerro Prieto it has been calculated that the reservoir temperature is 248°C and a vapor fraction 0.224 by weight with a two-flow approach. There is a difference of 30°C between the temperature obtained by applying the quartz solubility expression on the total discharge and the reservoir fluid silica concentration. The reservoir fluid is supersaturated with respect to quartz. On the other hand, the deep reservoir temperature can be calculated with the quartz solubility regression equation assuming the quartz-water equilibrium in the reservoir.

Acknowledgements- The work was carried out under the project MEX/8/022 financed by the IAEA, Vienna for 1997-98. The author appreciates the constructive comments and suggestions from Dr. A.H. Truesdell and an anonymous reviewer.

REFERENCES:

- Brisco H.V.A., Mathews J.W., Holt P.E. and Sanderson P.M. (1936-7) Some new characteristic properties of certain industrial dusts. *Inst. Min. Metall. Trans.*, Vol. 46, 291-302.
- Crerar D.A. and Anderson G.M. (1971) Solubility and solvation reactions of quartz in dilute hydrothermal systems. *Chem. Geol.*, Vol. 8, 107-122.
- Fausto J.J., Sánchez A., Jiménez M.E., Esquer I., and Ulloa F. (1979) Geoquímica hidrotermal del campo geotérmico de Cerro Prieto. Second Symp. Cerro Prieto geothermal field, Mexicali, Baja California, 199-223.
- Fleming B.A. and Crerar D.A. (1982) Silicic acid ionization and calculation of silica at elevated temperature and pH. Application to geothermal fluid processing and reinjection. *Geothermics*, Vol. 11, 15-29.
- Fournier R.O. (1977) Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, Vol. 5, 41-50.
- Fournier R.O. and Potter R.W. II (1982) A revised and expanded silica (quartz) geothermometer. *Geotherm. Resour. Counc. Bull.*, Vol. 11, 3-12
- Gerardo-Abaya J., Schueszler C. and Groening M. (1998) Results of the interlaboratory comparison for water chemistry in natural geothermal samples under RAS/8/075. Report. IAEA, Vienna, 18pp.
- Haar L., Gallagher J.S. and Kell G.S. (1984) NBS/NRC steam tables: thermodynamic and transport properties for vapor and liquid states of water in SI units. Hemisphere publishing corporation N.Y. 320pp.
- Henley R.W., Truesdell A.H., Barton P.B. and Whitney J.A. (1984) Fluid-mineral equilibria in hydrothermal systems. *Soc. Econ. Geol. El Paso, TX*, 267pp.
- Mahon W.A.J. (1966) Silica in hot water discharged from drillholes at Wairakei, New Zealand. *N.Z.J. Sci.* vol. 9, 135-144.
- Rimstidt J.D. (1997) Quartz solubility at low temperatures. *Geochim. Cosmochim. Acta*, Vol. 61, 2553-2558.
- Siever R. (1962) Silica solubility, 0° to 200°C., and the diagenesis of siliceous sediments. *J. Geol.*, Vol. 70, 127-150.
- Truesdell A.H. and Fournier R.O. (1977) Procedure for estimating the temperature of a hot water component in a mixed water by using a plot of dissolved silica versus enthalpy. *USGS J. Research*, Vol. 5, 49-52.
- Truesdell A.H., Thompson J.M., Coplan T.B., Nehring N.L., Janik C.J. (1979) The origin of the Cerro Prieto geothermal brine. Second Symp. Cerro Prieto geothermal field, Mexicali, Baja California, 224-240.
- van Lier J.H. de Bruyn P.L. and Overbeck T.G. (1960) The solubility of quartz. *J. Phys. Chem.*, Vol. 64, 1675-1682.
- Verma M.P. (1997) Thermodynamic classification of vapor and liquid dominated reservoir and fluid geochemical parameter calculations. *Geofísica Internacional*, Vol. 36, 181-189.
- Verma M.P. (1999) Chemical thermodynamics of silica: acritique on its geothermometer. *Geothermics*, Vol. 00, 1-24.
- Verma S.P. and Santoyo E. (1997) New improved equations for Na/K, Na/Li and SiO₂ geothermometers by outlier detection and rejection. *J. Volcanol. Geotherm. Res.* Vol. 79, 9-23.
- White D.E. Brannock W.W. and Murata K.J. (1956) Silica in hot-spring waters. *Geochim. Cosmochim. Acta*, Vol. 10, 27-59.

Table 1: The iteration process to calculate the deep reservoir temperature with considering quartz equilibrium conditions.

T (°C)	Enthalpy (J/g)			Y _{vap}	SiO ₂ (ppm)	
	Liq	Vap	Reser		Solubility	Mass Balance
250	1085	2802	1203.5	0.069	429.19	555.32
260	1134	2797	1203.8	0.042	472.94	539.67
270	1185	2890	1203.8	0.011	519.28	522.75
271	1190	2789	1202.8	0.008	524.06	521.17
272	1195	2788	1203.0	0.005	528.87	519.60
275	1210	2785	1202.1	-0.005	543.44	514.43

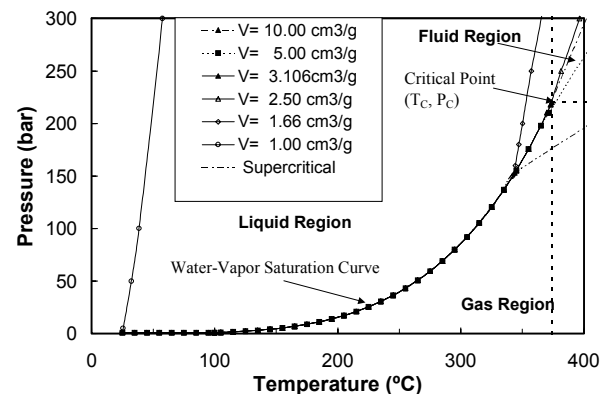


Figure 1: The PT characteristics of water for different total specific volumes in a closed vessel. The line corresponding to the "supercritical" represents the extension of the PT curve is for the case when the specific volume is equal to the critical volume (i.e. $V = 3.106 \text{ cm}^3/\text{g}$) in the supercritical region.

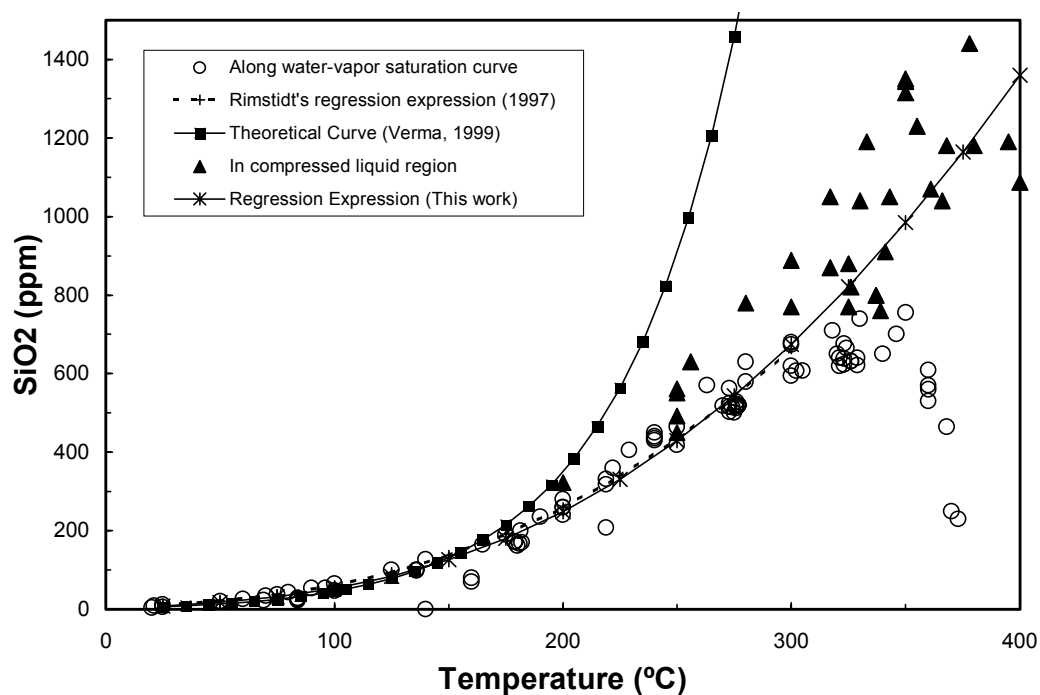


Figure 2: Experimental quartz solubility data along the water-vapor saturation curve and in the compressed liquid region

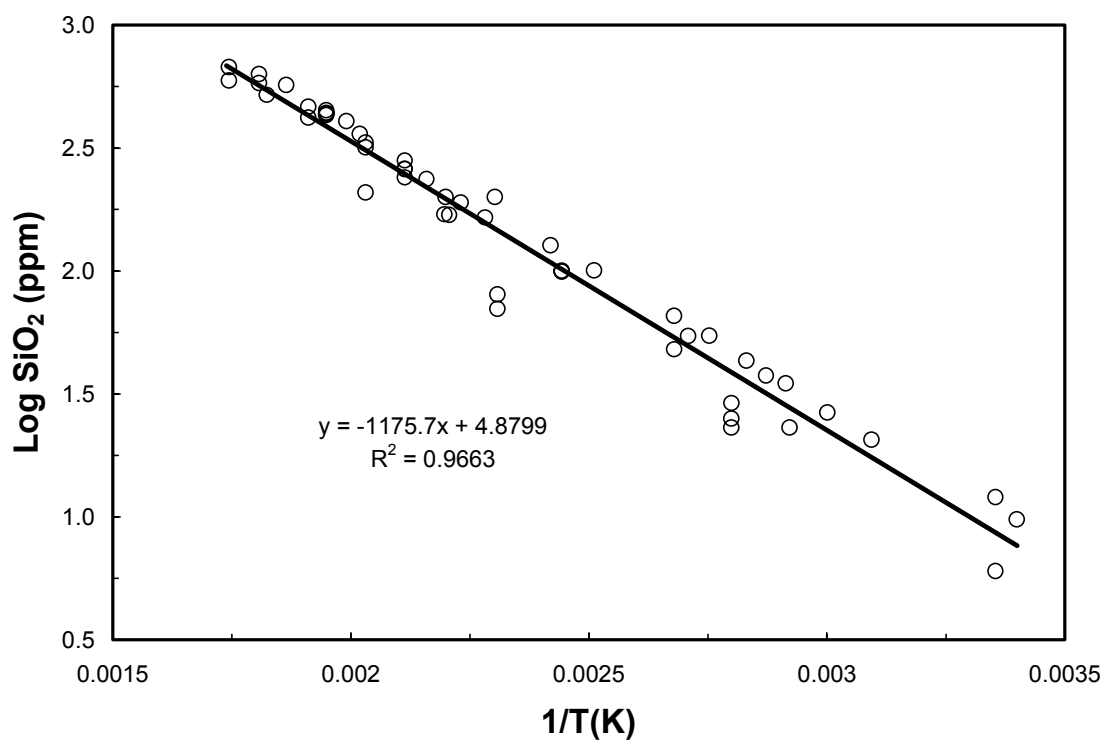


Figure 3: A regression relation for quartz solubility data along water-vapor saturation curve

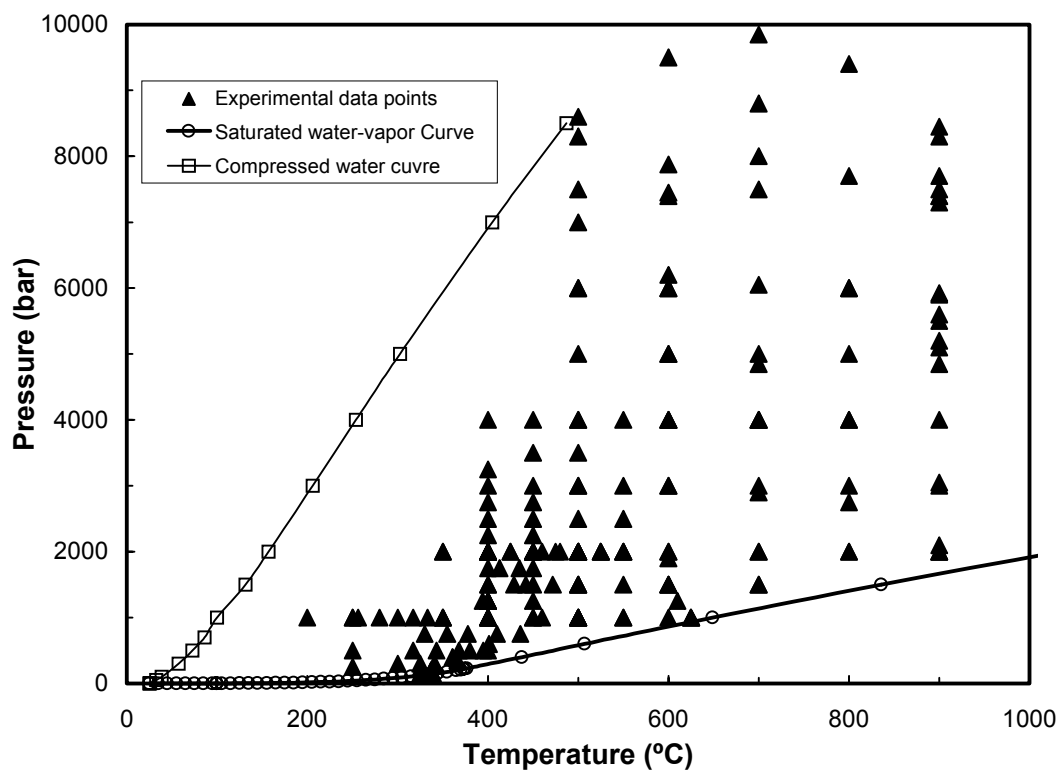


Figure 4: The pressure and temperature values for all the experimental determinations of quartz solubility data in the compressed liquid region together with the theoretical curves for the two extreme cases for existence of water in the reaction vessel.

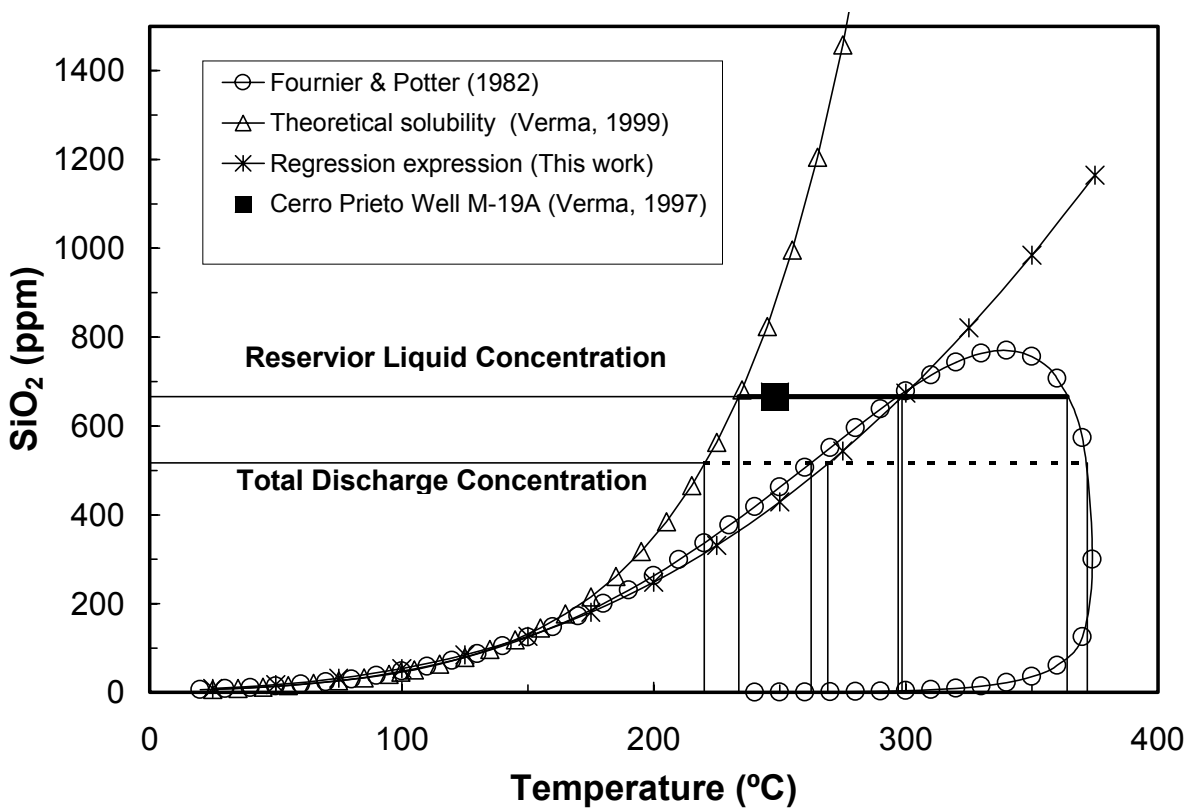


Figure 5: The calculated concentration of silica in the liquid phase in the reservoir and in the total concentration at wellhead for the well M-19A at Cerro Prieto (Verma, 1997). The reservoir temperature is 248°C. Therefore, the reservoir concentration of silica is higher than the experimental solubility values, but it is lower than the thermodynamically calculated value.